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The Removal and Recovery of Metals from Sludge and Sludge Incinerator Ash

Research Report No. 33

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RESEARCH REPORTS

These RESEARCH REPORTS describe the results of investigations funded under the Research Program for the Abatement of Municipal Pollution within the Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality. They provide a central source of information on the studies carried out in this program through in-house projects by both Environment Canada and the Ontario Ministry of the Environment, and contracts with municipalities, research institutions and industrial organizations.

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THE REMOVAL AND RECOVERY OF METALS FROM SLUDGE AND SLUDGE INCINERATOR ASH

by

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RESEARCH PROGRAM FOR THE ABATEMENT
OF MUNICIPAL POLLUTION WITHIN THE
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ABSTRACT

The electrochemical plating of Cu, Zn, Ni and Cd from aqueous solutions has been studied using standard plate type electrodes and improved efficiencies were attained with fluidized bed electrodes. Because direct electroplating from sludge was found to be inefficient, acid and base additions were made to solubilize the metals prior to plating.

Most of the metals and phosphorus in the digested sludge could be dissolved by adding sufficient H_2SO_4 or HCl to lower the sludge pH to 1.5. The average cost of acid required per ton of dry solids was $41 for the H_2SO_4 and $77 for HCl. Little economic advantage would be gained by recovering sludge constituents, since processing costs for the large volumes of dilute leachate would be high. Therefore, the removal of heavy metals from wet sludge to reduce their toxicity does not appear to be economically feasible.

The metals and phosphorus in sludge incinerator ash can be solubilized with H_2SO_4 in a countercurrent stepwise process which uses most of the acid. Further processing of the H_2SO_4 leachate for recovery of valuable constituents is complicated by the presence of large quantities of iron in the leachate. Neutralization of the leachate with NaOH precipitates all the metals and phosphorus. Treating this precipitate with a hot NH_4OH -$(NH_4)_2SO_4$ mixture resolubilizes most of the trace metals and phosphorus leaving iron oxide in the solid phase. Electroplating can remove Cu, Zn, Ni and Cd from the ammonia leach, and ammonium phosphate can be recovered from the solution after electrolysis. While processing costs for incinerator ash are much less that those for wet sludge, the procedure does not appear to be economically viable except for very large treatment plants.

RESUME

L'électrodéposition du cuivre, du zinc, du nickel et du cadmium provenant de solutions aqueuses a été étudiée à l'aide d'électrodes ordinaires en plaque; l'efficacité de ce procédé a été accrue en utilisant des électrodes en lit fluidisé. En raison du faible rendement de l'électrodéposition à partir de boues, des acides et des bases ont été ajoutés à ces dernières afin de solubiliser préalablement les métaux.

La plus grande partie des métaux et du phosphore contenus dans les boues digérées pourraient être dissoute par une addition de H_2SO_4 ou de HCL permettant d'abaisser le pH des boues à 1.5. Le coût moyen de l'acide utilisé par tonne de matières sèches était de $41 dans le cas du H_2SO_4 et de $77 pour le HCl. Du pointe de vue économique, la récupération des éléments contenus dans les boues n'offre que peu d'avantages en raison des coûts élevés du traitement des volumes importants de percolats dilués. Ainsi, l'extraction des métaux lourds, afin de réduire la toxicité des boues humides, ne semble pas économiquement réalisable.

Les métaux et le phosphore présents dans les cendres des incinérateurs de boues peuvent être solubilisés en présence de H_2SO_4, grâce à un procédé discontinu à contre-courant utilisant la plus grande partie de l'acide. La présence de quantités importantes de fer dans la solution de lixiviation au H_2SO_4 nuit au traitement ultérieur de cette solution afin d'en récupérer les éléments utiles. La neutralisation de cette solution à l'aide de NaOH fait précipiter tous les métaux et le phosphore. Le traitement de ce précipité au moyen d'un mélange chaud de NH_4OH et de $(NH_4)_2SO_4$, remet les métaux à l'état de trace et le phosphore en solution, tandis que l'oxyde de fer demeure à l'état solide. L'électrodéposition peut extraire le cuivre, le zinc, le nickel et le cadmium de la solution ammoniacale; on peut de plus récupérer le phosphate d'ammonium après l'électrolyse. Les coûts du traitement des cendres d'incinérateur sont beaucoup moins élevés que ceux du traitement des boues humides, mais le procédé ne semble pas économiquement viable sauf s'il est appliqué dans de trés grosses usines de traitement.

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CONCLUSIONS

Copper, zinc, nickel and cadmium have been successfully electroplated from aqueous solutions using copper struck graphite and aluminum electrodes. An improved current efficiency for metal plating was obtained using fluidized bed electrodes. Direct electroplating from digested sewage sludge was unsuccessful, so attention was focussed on leaching the metals from the sludge so they could be electroplated from the extracts.

Most trace metals, as well as phosphorus, could be solubilized from wet sludge by adding sufficient H_2SO_4 or HCl to reduce the pH of the sludge to 1.5. Average acid costs for the eight sludges studied were \$41 for H_2SO_4 and \$77 for HCl. If sludge detoxification by acid digestion followed by recovery of metals and phosphorus from the leachates was adopted, the costs of H_2SO_4 alone would more than double current sludge disposal costs. Little benefit would be attained from the recovery of phosphorus or trace metals from this dilute raw material because of high processing expenditures.

Sulphuric acid can be used to non-selectively solubilize metals and phosphates from sludge incinerator ash. Further processing of the acid extract for recovery of valuable trace metals and phosphorus is complicated by the presence of high concentrations of iron in the extract. Neutralization of the H_2SO_4 leachate with NaOH, followed by treatment of the resulting precipitate with NH_4OH - $(NH_4)_2SO_4$ redissolves the copper, zinc, nickel, cadmium and phosphate, leaving iron oxide in the solid phase. Further electrochemical processing of the NH_4OH - $(NH_4)_2SO_4$ extract permits recovery of Cu, Zn, Ni and Cd. The final product shown in the process flow chart (Figure 16) is a concentrated solution of ammonium phosphate. An order of magnitude cost evaluation of the process indicates that it is probably not economically feasible except for very large treatment plants.

RECOMMENDATIONS

The best method for disposing of wet sludge and making use of its valuable constituents is to spread it on agricultural land. Unfortunately, because of high concentrations of some heavy metals in sludge from industrialized areas, this method poses severe environmental hazards. It has been shown that recovery of toxic trace metals from wet sludges is not economically feasible. Elimination of metal discharges into sewers at the source is apparently the only practicable solution. More stringent controls are necessary to curb the industrial discharge of metals into municipal sewage systems.

This report shows that changing the sludge incineration temperature has a considerable effect on the leachable metals and phosphorus in the ash. Experiments on the effect of various incineration parameters on the leachability of ash constituents should be undertaken. Then, by a judicious choice of incineration conditions, any municipality would be able to minimize the environmental impact of landfilling sludge incinerator ash.

The recovery of phosphates and metals from incinerator ash should be attempted only when a positive economic benefit can be accrued. The method for recovery of phosphates and metals described in this report does not appear to be economically viable except for very large plants. Further experimentation is recommended on direct NH_4OH - $(NH_4)_2SO_4$ leaching of the ash at high temperatures and pressures, such as those employed in the mining industry (29, 30). This may lead to a cheaper method of extraction.

1. INTRODUCTION AND OBJECTIVES

Considerable quantities of heavy metals are present in raw sewage (1, 2, 3). In general, the higher the industrial load to the sewage treatment facility, the higher will be the trace metal concentration in the influent, although metals are also present in domestic sewage and surface runoff (4). Conventional sewage treatment processes remove 50-80% of most metals from raw sewage and concentrate them in the sludge (5, 6). Anaerobic or aerobic digestion of the sludge can further increase the metal concentration. For treatment facilities which receive large quantities of industrial effluents, the metal concentration in digested sludge can reach quite high levels.

About half of the sludge produced in Ontario is disposed of by spreading on agricultural land. The other half is incinerated by three of the largest cities in the province: Toronto, Hamilton and London (7). The disposal of sludge on agricultural land to take advantage of its nutrient content can present problems, since studies have shown that repeated applications can result in metal toxicity to plants (8, 9, 10) and enhancement of toxic metal levels in consumable crops (11, 12). The landfilling of sludge incinerator ash may also pose a hazard if the heavy metals are present in the ash in leachable forms. Thus, methods for removing and recovering metals from sludge and sludge incinerator ash are needed.

Two recent feasibility studies on this subject have been reported. Scott and Horling (13) studied the extraction and recovery of phosphorus and iron together with a few other metals from the sludge and filter cake produced at the North Toronto Sewage Treatment facility. The removal of metals and phosphorus from the sludge was effected by digestion with sulphuric acid and a cursory study on the recovery of iron and phosphorus from the acid leachate was also performed. Treatment cost estimates were $30-35 per million gallons of sewage influent with about $10 regained by recovering iron and phosphorus, resulting in a net treatment cost of $20-25 per million gallons of influent.

Cambrian Processes Limited (14) performed experiments on Toronto sludge incinerator ash. Several leaching techniques for solubilizing metals and phosphorus in the ash were studied and their data

indicated that heavy metals leach out of the ash, even with neutral distilled water. The procedure finally recommended involved leaching with 60% sulphuric acid, followed by various recovery stages which included ion exchange. It was concluded that, at present, only phosphorus recovery seems economically warranted, but since there are indications that the ash in its present form may contribute to heavy metal loading of groundwater, the study of recovery processes should be expanded.

A more detailed examination of removal and recovery processes seemed warranted and it was apparent that the application of standard electrochemical techniques to this problem could prove fruitful. Kuhn (15) has summarized recent advances in the application of electrodialysis, electroflotation, electrooxidation and electroreduction for the treatment of aqueous effluent streams. Since the writing of that article, electroprecipitation of phosphate from sewage using dissolving metal anodes and the treatment and disinfection of wastewater-seawater mixtures by electrolysis has been reported (16, 17). Although an electroflotation process has been used for sewage sludge thickening (18), no known attempt has been made to use electrochemical methods to remove metals from digested sewage sludge.

Copper, zinc, cadmium, nickel, tin, lead and chromium can all be electroplated from aqueous solutions of their salts (19). The efficiencies at which these metals plate is very much a function of the solution composition, and interference by impurities is common. Although the direct electrolysis of sludge mixtures would seem to be an attractive approach for removal of metals, the complexity of the sludge may make this process hopelessly inefficient. Two major problems which arise involve the effect of organic matter upon the electrolysis and the availability of metals in the sludge. The anodic oxidation of many types of organic compounds has been reported (20, 21) so the presence of organic materials may reduce the efficiency of the metal plating process. The second problem, the availability of metals, is more fundamental. Since the electrodeposition would occur for dissolved metals, and most of the metals in sludge are in the solid phase, the efficiency of the plating process would depend on the rates of dissolution of the metals of interest. Metals in the solid phase would be in

equilibrium with the dissolved species, so removal of dissolved metals by electrodeposition should lead to a shift in equilibrium and metal solubilization. Whether or not this solubilization occurs at a rate which would make the direct electrodeposition of metals from sludge practical would depend on the character of the sludge.

If either of the two above interferences should make the direct electrolysis of sludge impractical, it would become necessary to treat the sludge to dissolve more metals and then to separate the sludge from the metal-containing extract. Electrochemical treatment of the extract could then be performed. Since chemical treatment which solubilizes metals may also solubilize phosphates, some effort should be made to recover phosphorus in an economically valuable form to offset, at least partially, the cost of chemical treatment.

Previous investigations into this subject (13, 14) have dealt with one type of sludge and one type of sludge incinerator ash. Since sewage treatment procedures vary for different facilities, and different methods of sludge conditioning and phosphorus removal are used, it is possible that metal recovery may be more efficient from one type of sludge than another. Similarly, factors such as incineration temperatures may effect the leachability of metals in incinerator ash. Therefore, it is imperative to conduct a recovery study on as many different types of sludge and ash as possible. Samples of digested sludge were collected from eight activated sludge sewage treatment facilities in Southern Ontario. Sludge ash samples which had been incinerated at various temperatures were also obtained. Table 1 shows the treatment facilities from which sludges and ashes were obtained, together with details about treatment procedures. An experimental program was designed to systematically investigate metal removal and recovery from these samples.

TABLE 1

SEWAGE TREATMENT FACILITIES FROM WHICH SLUDGES AND ASHES WERE COLLECTED

FACILITY	PHOSPHORUS REMOVAL CHEMICALS ADDED	SLUDGE DIGESTION OR INCINERATION PROCEDURE
Oakville	none	anaerobic
Markham	none	anaerobic
Aurora	none	aerobic (polymer conditioned)
Newmarket	lime	anaerobic
Guelph	alum	anaerobic
Fergus	iron	anaerobic
Brantford	iron	anaerobic
Dunnville	iron	anaerobic

TABLE 1 (CONTINUED)

Hamilton	none+	Incineration (820-870°C)
London	none	Multiple Hearth Incineration (#1 480-540°C, #2 600°C, #3 840°C, #4 980°C, #5 870°C, #6 320°C)
Hamilton*	none+	Incineration* (760°C)
Hamilton*	none+	Incineration* (820°C)
Hamilton*	none+	Incineration* (870°C)
Hamilton*	none+	Incineration* (930°C)
Borden*	alum	Incineration* (760°C)

+ Hamilton does not add any chemicals for phosphorus removal because its influent is already high in iron. The sludge produced at this plant is iron rich.

* These sludges were incinerated in the Environmental Protection Service experimental incinerator at Borden, Ontario.

2. EXPERIMENTAL

2.1 Electrochemical Procedures

Two electrochemical cells were used in this project and are shown in Figures 1 and 2. In the single compartment cell (Figure 1), a platinum gauge cathode and a Pt spiral anode are shown but other electrodes, e.g. graphite rods, were also used. In the dual compartment cell (Figure 2), the anode and cathode are separated by a sintered glass frit. In some experiments, a fluidized bed of 20-40 mesh granular graphite, copper or aluminum was employed as the cathode. In others, simple plate type lead, iron and aluminum electrodes were used.

Preconditioning is necessary before successful electrodeposition can occur on aluminum electrodes (22). The Al plates or granules are first etched for 2-5 min. in 25% H_2SO_4 at 83°C to remove undesirable microconstituents. An oxide layer of uniform thickness is then formed by immersion in 50% HNO_3. The electrode is then dipped in an alkaline zincate solution (400-500 g/l NaOH, 80-100 g/l ZnO), where a displacement reaction takes place which covers the electrode with a thin layer of zinc metal. A copper strike may then be applied over this zinc layer (or onto any of the other electrode materials) by immersing the electrode into a Rochelle type copper cyanide solution (41.3 g/l CuCN, 48.8 g/l NaCN, 30.0 g/l Na_2CO_3, 60.0 g31 $KNaC_4H_4O_6 \cdot 4H_2O$) and applying a potential of about -1.5 V to the electrode for 2-5 min.

All potentials given are relative to a saturated calomel reference electrode which was used in both the single and dual compartment cells. A Princeton Applied Research (PAR) Model 173 Potentiostat/Galvanostat was used to regulate the voltage applied across the cell and to measure the resulting current flowing between the electrodes. In the three electrode systems the potentiostat maintains a constant potential between the reference electrode and the working electrode by varying the voltage applied to the counter electrode. This procedure compensates for any current resistance (IR) drop taking place within the solution as a result of current flowing through it.

Static experiments on known volumes of stirred liquid were performed in both cells and samples were withdrawn at various time intervals

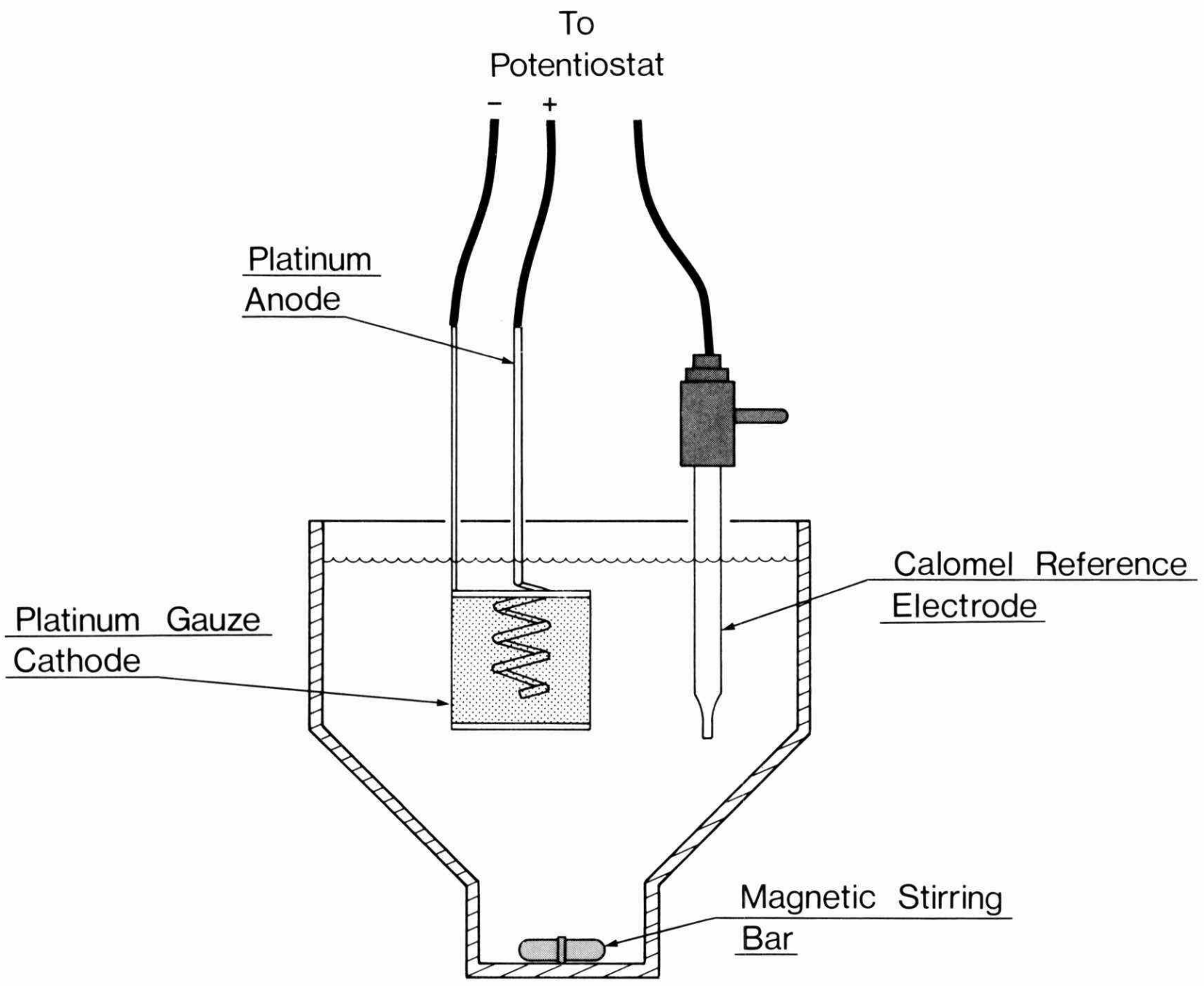

FIG. 1 SINGLE COMPARTMENT ELECTROCHEMICAL CELL

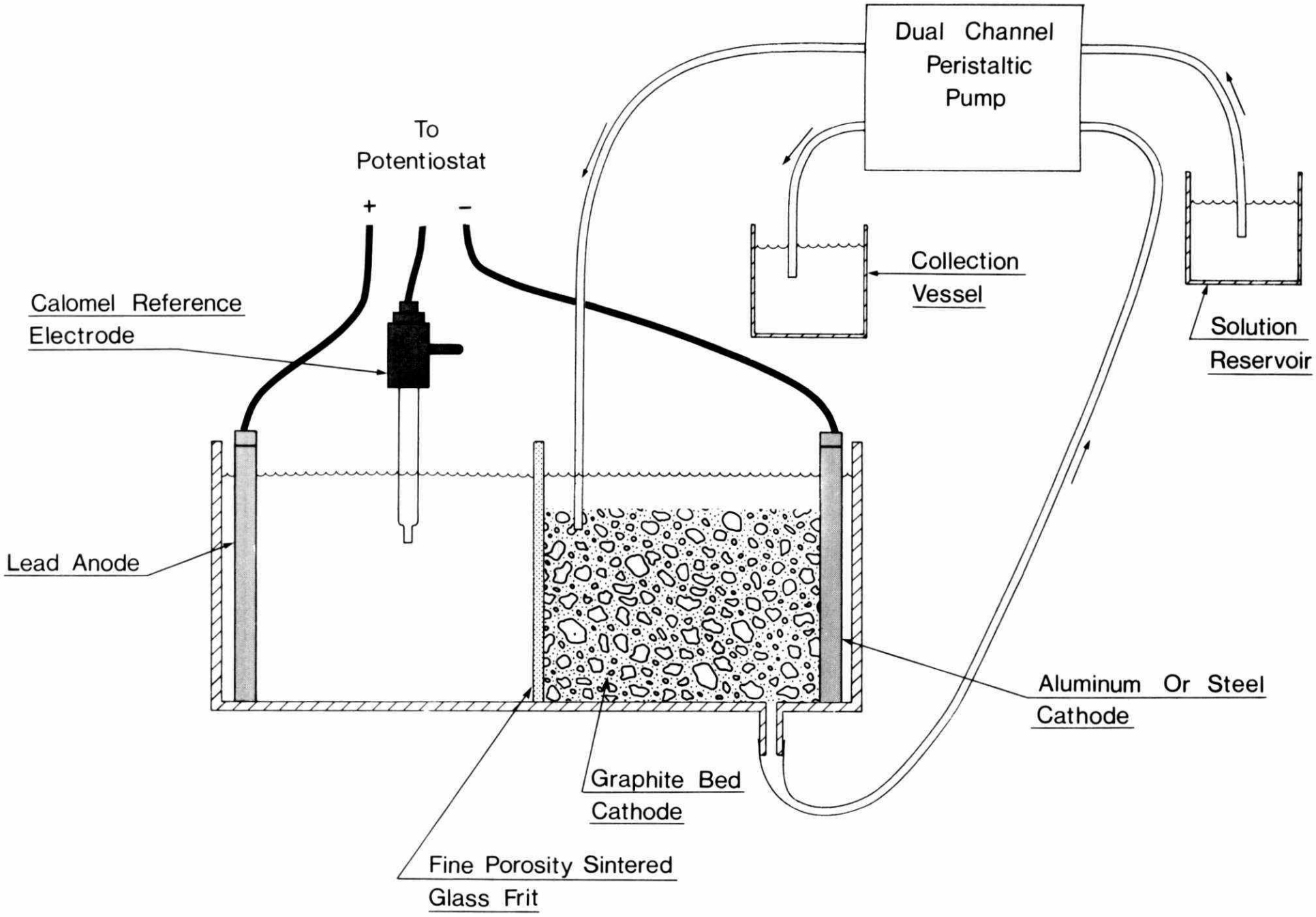

FIG. 2 DUAL COMPARTMENT ELECTROCHEMICAL CELL

for analysis. When the fluidized bed was used as a cathode, solutions were pumped through the bed at various flow rates using a peristaltic pump and samples of the effluent were taken for analysis.

2.2 Analytical Methods

The total metal content of each sludge was determined by digesting a 10 ml aliquot of sludge in a mixture of 20 ml concentrated HCl and 6 ml concentrated HNO_3. After the sample had been boiled down to between 5 and 10 ml, the digestion was repeated. In some cases, solids were still present after this second digestion, but a complete HF-$HClO_4$ digestion on several of these solid residues showed that virtually all the metal bed had been solubilized. Finally, the concentrate was diluted to about 25 ml and filtered through Whatman No. 42 filter paper and the filtrate made up to a volume of 50 ml. The total metal concentration in the leachate was then determined using standard atomic absorption techniques (23) on a Perkin-Elmer Model 403 Atomic Absorption Spectrophotometer equipped with a deuterium background corrector. For the incinerator ash, total digestion was accomplished using an HF-HNO_3-$HClO_4$ acid mixture in a teflon bomb at 140°C (23). Recovery studies, performed by spiking the solutions and by digesting standards using the above procedures, gave quantitative return of the metals. Sample analysis for total phosphorus, ammonia nitrogen and total organic carbon were made using standard techniques (23, 24).

The total available or leachable metal in the sludges and sludge incinerator ashes was measured using the acetic acid extraction procedure described by Van Loon (25). Ten ml of 0.5 N acetic acid was added to 0.5 - 1.0 g of sludge residue or incinerator ash and this mixture was digested at medium heat until almost dry. Another 2 ml of 0.5 N acetic acid was added and the sample evaporated to dryness. The sample was cooled, dissolved in 1 ml of 0.5 N acetic acid, filtered into a 25 ml flask, and diluted with distilled water. The metal levels were then determined by atomic absorption.

2.3 Leaching Procedures

Sludge acid leaching experiments were carried out by taking 50 ml of sludge, titrating with either HCl, HNO_3 or H_2SO_4 until the desired pH was reached, and then shaking the sample for 1 hr on a wrist action shaker. The sample was then filtered through Whatman No. 42 filter paper and diluted to 100 ml. The total digestion procedure described above was then performed on the filter paper residue so that the percentage extraction could be calculated. Basic leaching experiments were done by adjusting the pH of 50 ml of sludge with a solution of 1 M NH_4OH - 4 M $(NH_4)_2SO_4$. The $(NH_4)_2SO_4$ is added to increase the free ammonia concentration in the solution. After shaking, filtration and dilution, it is imperative that the pH of this basic leachate solution be reduced to 1 or 2 by the addition of acid (HNO_3) or spurious analytical results will be obtained.

Leaching experiments were performed on 1 g samples of ground sludge incinerator ash (-80 mesh) with 25 ml of leachate. Samples were refluxed, diluted to 1/5, filtered and finally made up to 200 ml before analysis.

3. RESULTS AND DISCUSSION

3.1 Electrochemical

Preliminary experiments on copper plating were carried out using 100 ml salt solutions in the single compartment cell. It was found that copper could be plated out of a neutral or acidic copper sulphate solution at a potential of -1.5 volts. To test what effect sludge impurities would have on the plating process it was decided to add a mixture of ferric and ferrous salts to the copper solutions, since iron is a major constituent of sludge. The addition of iron drastically reduced the efficiency of copper plating. Most of the current flowing in the cell was being consumed to reduce ferric to ferrous at the cathode and then reoxidize it back to ferric at the anode.

$$Fe^{3+} + e \underset{\text{anode}}{\overset{\text{cathode}}{\rightleftharpoons}} Fe^{2+} \qquad (1)$$

For this reason, experimentation with the single compartment cell was abandoned and further experiments were carried out using the dual compartment cell, where the anode and cathode compartments were separated by a sintered glass frit. In this cell, a simple heavy metal free salt solution could be used to conduct current in the anode compartment and the plating solution of interest could be added only to the cathode compartment. Some of the current would still be consumed to reduce any Fe^{3+} in the solution to Fe^{2+} at the cathode, but once the Fe^{3+} had been reduced, plating of the metals such as copper would proceed normally.

The electrochemical experiments were focussed on four trace metals, copper, zinc, nickel, and cadmium, because these metals are potentially recoverable by electrochemical methods and also because sludge toxicity problems have been traced mainly to these elements (10, 11). Plating experiments were performed in the dual compartment cell on solutions of approximately 1000 ppm metal sulphate in the supporting electrolyte 0.5 M $(NH_4)_2SO_4$. Plating was also attempted from acidic media using metal sulphate solutions in 0.5 N H_2SO_4. A lead plate in a 250 ml solution of 0.5 M $(NH_4)_2SO_4$ was used in the anode compartment and

a zinc dipped, copper struck aluminum plate or copper struck graphite rods were used as plating electrodes in the cathode compartment. The plating potentials used, -1.5 volts for copper and -3.5 volts for zinc, nickel and cadmium, are those recommended for industrial plating processes by Potter (19). The results of the electrolysis of 250 ml samples of copper, zinc, nickel and cadmium sulphate solutions are shown in Tables 2, 3, 4 and 5.

It is apparent that all four metals could be readily plated from neutral salt solutions but that only copper and cadmium could be plated from a strongly acidic media. The current efficiency (percentage of the quantity of electricity passing through the cell which is used in producing the final yield of electrolytic product) and the energy efficiency (kilowatt hours of power required per pound of metal plated) are recorded in Table 6. The current efficiency is highest for copper. Also, both copper and cadmium are more efficiently plated from neutral solutions than they are from acidic solutions. The current efficiency is lower for 95% metal removal than for 75% metal removal because as the metal concentration in the cell is reduced, the current efficiency is reduced.

One important point that must be noted is that zinc, nickel and cadmium cannot be plated from a solution containing high levels of copper. Any scheme that is proposed for electroplating from solutions containing all four metals must involve two stages. In the first stage, copper would be plated out at -1.5 volts and then in the second stage, the other three metals could be plated out together at -3.5 volts. To test this final hypothesis a plating experiment was carried out on a mixed solution containing only zinc, nickel and cadmium at the approximate levels at which they are normally found in sludges. The results of this experiment are shown in Table 7. It can be seen that all three metals can be simultaneously plated from this copper-free solution at -3.5 volts.

The final electrochemical experiments that were performed on the metal salt solutions tested fluidized bed or porous flow through electrodes to see if current efficiencies for metal removal could be improved. These types of electrodes have already been used by Bennion

TABLE 2

THE ELECTROLYSIS OF 250 ml OF ≃1000 ppm $CuSO_4$ IN 0.5 M $(NH_4)_2SO_4$ AND IN 0.5 N H_2SO_4 AT -1.5 VOLTS ONTO A COPPER STRUCK ALUMINUM ELECTRODE

	0.5 M $(NH_4)_2SO_4$		0.5 N H_2SO_4	
TIME (min)	COPPER CONC. (ppm)	CURRENT (milliamps)	COPPER CONC. (ppm)	CURRENT (milliamps)
0	929	200	882	220
10	750	180	713	210
20	668	170	610	210
30	570	150	485	210
40	398	145	378	205
50	325	125	283	200
60	250	120	193	200
80	138	100	98.0	200
100	60.5	90	53.5	195
120	31.5	80	25.6	190
150	11.0	60	8.5	180
180	4.0	50	2.6	170

TABLE 3

THE ELECTROLYSIS OF 250 ml OF ≃1000 ppm $ZnSO_4$ IN 0.5 M $(NH_4)_2SO_4$ AND IN 0.5 N H_2SO_4 AT -3.5 VOLTS ONTO A COPPER STRUCK ALUMINUM ELECTRODE

	0.5 M $(NH_4)_2SO_4$		0.5 N H_2SO_4	
TIME (min)	ZINC CONC. (ppm)	CURRENT (milliamps)	ZINC CONC. (ppm)	CURRENT (milliamps)
0	940	385	940	500
10	740	375		
20	563	375		
30	375	380	940	485
40	235	380		
50	130	380		
60	71	380	940	470
80	19	380		
100	7.0	375	940	460
120	2.8	375		
150	1.0	370	935	450

TABLE 4

THE ELECTROLYSIS OF 250 ml OF ≃1000 ppm $NiSO_4$ IN 0.5 M $(NH_4)_2SO_4$ AND IN 0.5 N H_2SO_4 AT -3.5 VOLTS ONTO A COPPER STRUCK ALUMINUM ELECTRODE

	0.5 M $(NH_4)_2SO_4$		0.5 N H_2SO_4	
TIME (min)	NICKEL CONC. (ppm)	CURRENT (milliamps)	NICKEL CONC. (ppm)	CURRENT (milliamps)
0	933	420	976	600
10	800	420		
20	665	420	963	510
30	575	420		
40	490	420	925	505
50	425	425		
60	353	425		
80	223	430	893	505
100	159	430		
120	129	420	888	505
150	64	420		
180	32	420		
210	20	415		

TABLE 5

THE ELECTROLYSIS OF 250 ml OF ≃1000 ppm $CdSO_4$ In 0.5 M $(NH_4)_2SO_4$ AND IN 0.5 N H_2SO_4 AT -3.5 VOLTS ONTO A COPPER STRUCK ALUMINUM ELECTRODE

	0.5 M $(NH_4)_2SO_4$		0.5 N H_2SO_4	
TIME (min)	CADMIUM CONC. (ppm)	CURRENT (milliamps)	CADMIUM CONC. (ppm)	CURRENT (milliamps)
0	1088	370	1020	620
10	890	370	870	560
20	635	370	730	500
30	445	370	578	500
40	240	370	410	500
50	174	370	315	495
60	96.5	370	221	490
80	42.3	370	133	470
100	18.1	370	74.0	470
120	7.9	365	47.5	460
150	2.0	350	21.5	455
180	0.3	340	12.6	450
250			2.9	425

TABLE 6

CURRENT AND ENERGY EFFICIENCY FOR THE ELECTROPLATING OF COPPER, ZINC, NICKEL AND CADMIUM FROM 1000 ppm SOLUTIONS

METAL	CURRENT EFFICIENCY FOR 75% REMOVAL	ENERGY EFFICIENCY FOR 75% REMOVAL (kWh/lb)	CURRENT EFFICIENCY FOR 95% REMOVAL	ENERGY EFFICIENCY FOR 95% REMOVAL (kWh/lb)
copper (neutral)	91%	0.64	75%	0.77
copper (acid)	69%	0.83	47%	1.2
zinc (neutral)	57%	2.3	41%	3.2
nickel (neutral)	28%	5.1	17%	8.6
cadmium(neutral)	41%	1.9	27%	2.8
cadmium(acid)	18%	4.2	11%	6.7

TABLE 7

THE ELECTROLYSIS OF Zn, Ni AND Cd SULPHATE SOLUTIONS IN 0.5 M $(NH_4)_2SO_4$ AT -3.5 VOLTS ONTO A COPPER STRUCK ALUMINUM ELECTRODE

TIME (min)	ZINC CONC. (ppm)	NICKEL CONC. (ppm)	CADMIUM CONC. (ppm)	CURRENT (milliamps)
0	940	41.4	10.2	355
10	850	33.0	8.8	360
30	330	16.3	4.1	360
60	33.1	2.5	0.5	345
90	1.1	0.2	0.1	325

and Newman (26) to remove copper from aqueous solutions. Copper solutions in 0.5 M $(NH_4)_2SO_4$ were pumped through the cathode compartment of the graphite filled dual compartment cell (Figure 2) at various flow rates. Sampling of the cell output was continued until the copper in the sample reached a constant value. The results are summarized in Table 8.

TABLE 8

THE ELECTROLYSIS OF $CuSO_4$ IN 0.5 M $(NH_4)_2SO_4$ AT -1.5 VOLTS USING A GRAPHITE BED ELECTRODE

FLOW RATE (ml/min)	STARTING CONC. (ppm)	FINAL CONC. (ppm)	CURRENT (ma)	CURRENT EFFICIENCY	ENERGY EFFICIENCY (kwh/lb Cu
14.2	948.4	206.7	595	90%	0.64
11.5	971.5	53.7	540	99%	0.58
9.5	948.4	< 0.01	500	91%	0.63

The solution volume put through the cell before a constant copper level was obtained was considerably higher than the volume required to flush the cell. A plot of current efficiency versus copper concentration (Figure 3) helps to explain this phenomenon. Curve 1 shows the electrolysis of copper using graphite rods without copper strike. It can be seen that the current efficiency is low at the start of the electrolysis (high copper concentration) but climbs to over 90% once the graphite rods have been thoroughly coated with copper. A similar experiment with copper struck graphite rods (curve 2) shows that the current efficiency is high (over 90%) right from the beginning of the electrolysis. The induction period for the graphite bed is, therefore, explained as the time required to deposit a coat of copper on the graphite particles. Copper striking of the bed prior to electrolysis would eliminate this problem. In both graphite rod experiments it can be seen (Figure 3) that the current efficiency drops dramatically as the copper concentration in the solution is reduced. Curve 3 on the graph and Table 8 reveal that the most impressive characteristic of the graphite bed electrode is that the current efficiency is independent of concentration. The copper concentration in a solution can be reduced to virtually zero

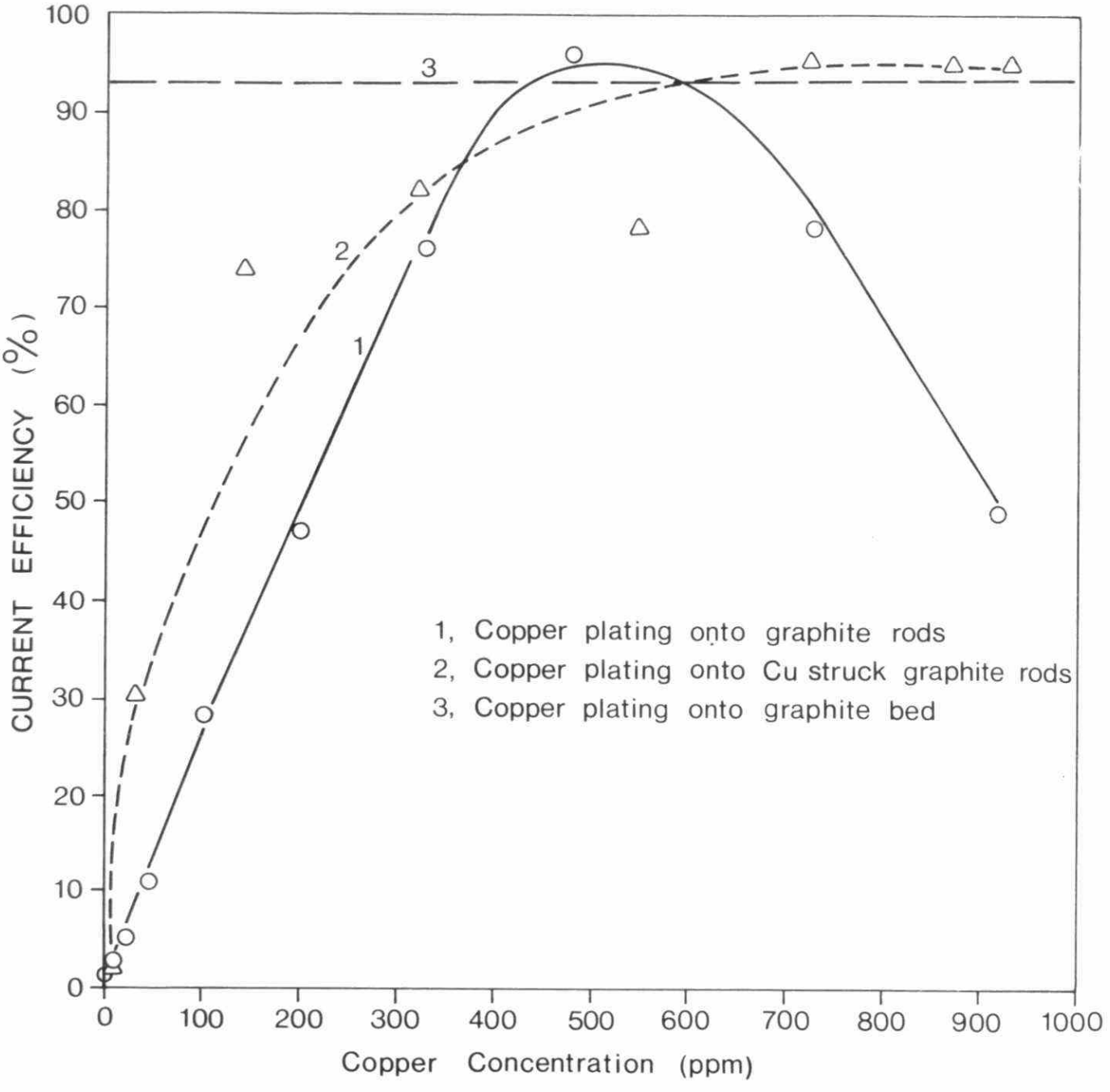

FIG. 3 CURRENT EFFICIENCY FOR ELECTROPLATING COPPER ONTO GRAPHITE AS A FUNCTION OF Cu CONCENTRATION

without a significant loss in current efficiency. There is little doubt that fluidized bed electrodes provide the best answer for the electrochemical metal removal from clear aqueous solutions. Zinc, nickel and cadmium could also be plated using this type of cell at -3.5 volts, and granular copper or granular aluminum (zinc dipped and copper and copper struck) could be used as electrode materials if desired.

Electrochemical plating directly from wet sewage sludge was attempted. Sludges (250 ml) were placed in the cathode compartment of the dual compartment cell and plating attempted onto a copper struck aluminum plate electrode. A number of voltage settings up to -5 volts were tried. Unfortunately, the quantities of metals removed from the sludges by this technique were extremely small. Therefore, it was decided that the only feasible approach for metal removal would be to first solubilize the metals chemically and then try to recover them from the extract. A systematic investigation was undertaken to totally or selectively solubilize the sludge constituents with various acids, bases and complexing agents.

3.2 Sludge Leaching

Solubilization of the metals in wet sludge samples was first attempted with the common mineral acids H_2SO_4, HCl and HNO_3. Known volumes of acid were titrated into the samples and the pH of the mixtures measured. Figure 4 shows a plot of pH (right axis) and of % Cd, Fe, Ni and Zn extraction (left axis) versus added volume of 1 N H_2SO_4 The pH of the sludge drops down quickly as the first acid is added then levels off, approaching zero asymptotically. Almost identical pH curves were obtained for HCl and HNO_3 (Figures 5 and 6, respectively). The extraction curves for the metals in Figure 4 rise quickly with small acid additions and eventually reach a plateau. Small differences between the extraction efficiency of H_2SO_4, HCl and HNO_3 (Figures 4, 5 and 6) are apparent but the shape of the extraction curves is virtually the same for all acids.

The choice of the best acid for extraction seemed quite open at this point. No dramatic differences between the acids were apparent for Oakville sludge and experiments with the other seven sludges also

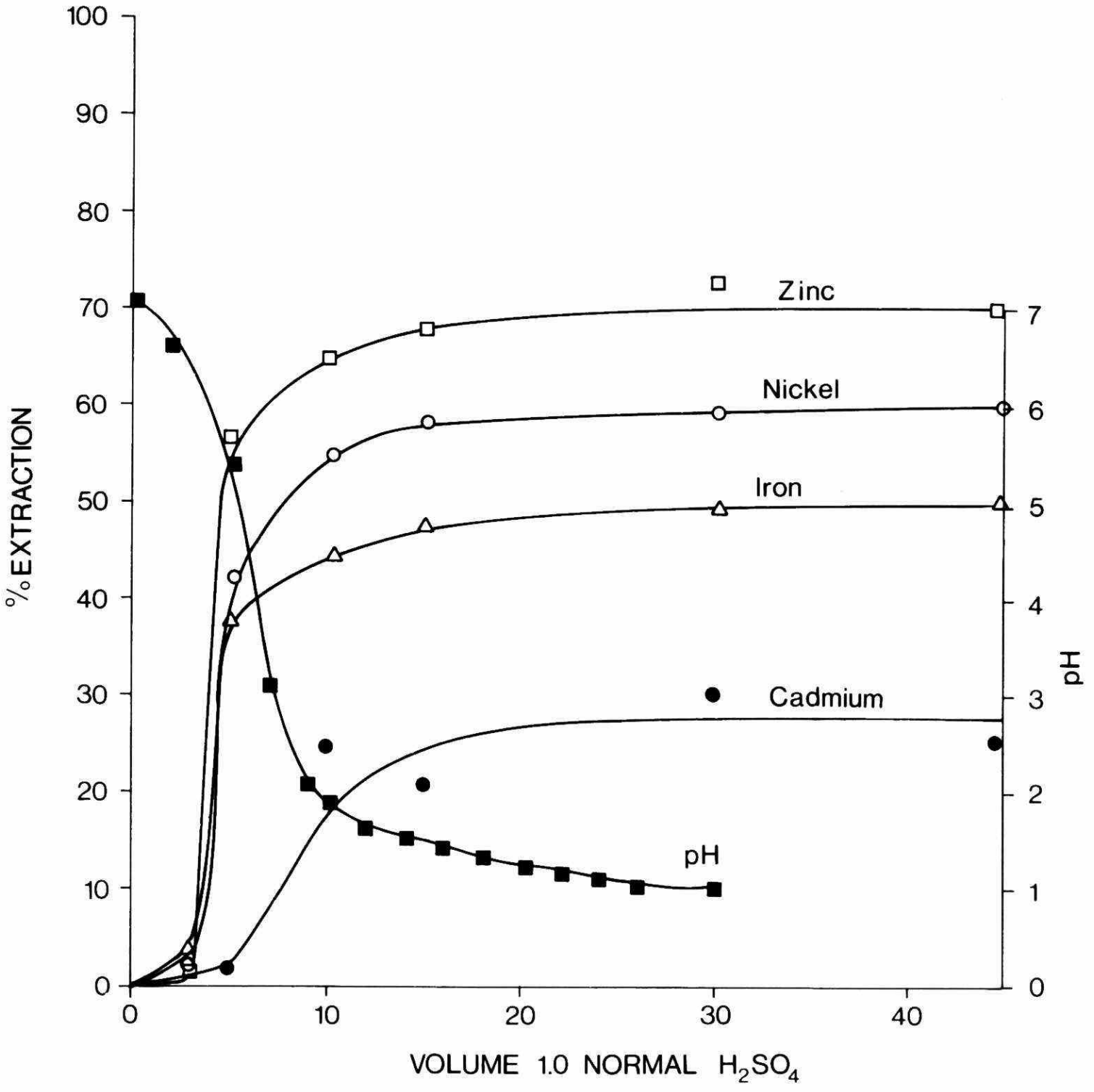

FIG. 4 METAL SOLUBILIZATION FROM OAKVILLE SLUDGE WITH H_2SO_4

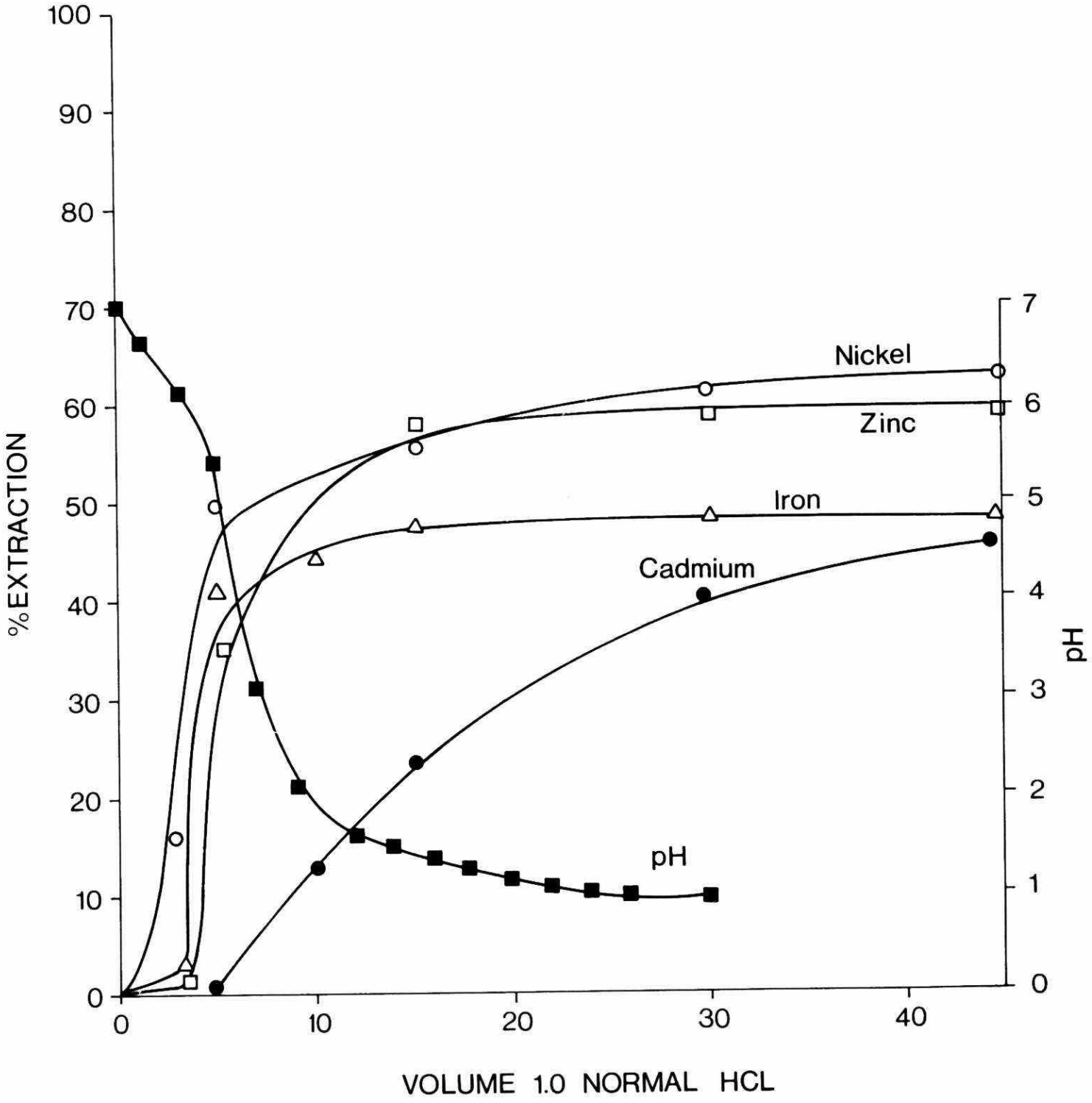

FIG. 5 METAL SOLUBILIZATION FROM OAKVILLE SLUDGE WITH HCL

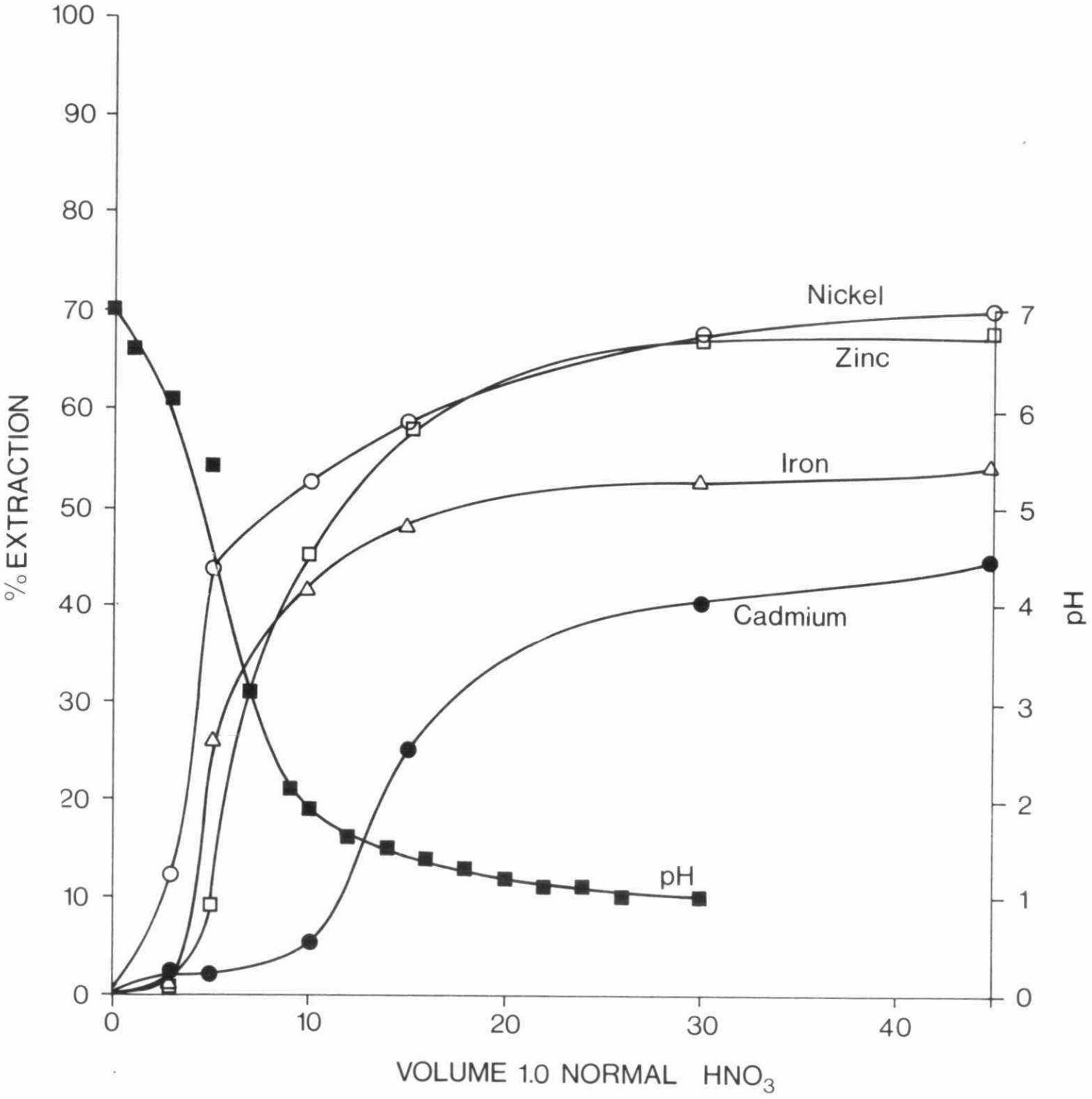

FIG. 6 METAL SOLUBILIZATION FROM OAKVILLE SLUDGE WITH HNO_3

showed little advantage for one acid versus another. Therefore, it was decided to eliminate HNO_3 from further study because of its high cost and also because nitrogen is know to pose eutrophication problems if discharged to aqueous environments (27).

Extraction and pH curves for the H_2SO_4 leaching of the seven other sludges studied are shown in Figures 7-13. The HCl extraction behaviour was similar so those plots are not included. Significant differences in the pH curves are apparent for the sludges, most notably for the lime sludge from Newmarket. However, all the pH curves level off at higher acid additions due to the strong buffering capacity of the sludges. The metal extraction curves reach an upper limit at the same time as the pH curves reach a lower limit. In all cases, by the time the pH of the sludge has reached 1.5 the metal extraction curves have reached a plateau.

Based on these data, the procedure adopted for acid extraction of the sludges was to add sufficient H_2SO_4 or HCl to lower the pH of the sludge to 1.5. This was followed by vacuum filtration of the sludges to separate the solids from the leachate. The residue was then rinsed with an equal volume of H_2O to restore normal pH. The solids could then be disposed of on agricultural land and the leachate further processed for the recovery of valuable constituents. Tables 9 to 16 show the initial sludge analyses and the percentage of the various sludge constituents removed by the acid extraction. Large differences in the treatment efficiency can be noted for the various sludges. One reason for this may be that constituents are present at variable concentrations, and depending on source and treatment, elements probably occur in different compounds and complexes. About 50-80% of most of the toxic metals (Cd, Cr, Ni Zn) were solubilized, but usually a negligible amount of copper and only small amounts of lead were extracted. About 75% of the phosphorus, 30% of the nitrogen and 10-15% of the organic carbon were leached by the acid. In general, the copper extraction paralleled the organic carbon. In cases where a high percentage of organic carbon was leached, the copper extraction percentage was also high and when less than 10% of the organic carbon was leached, copper extraction was usually less than 1% efficient. This behaviour may imply that much of the copper

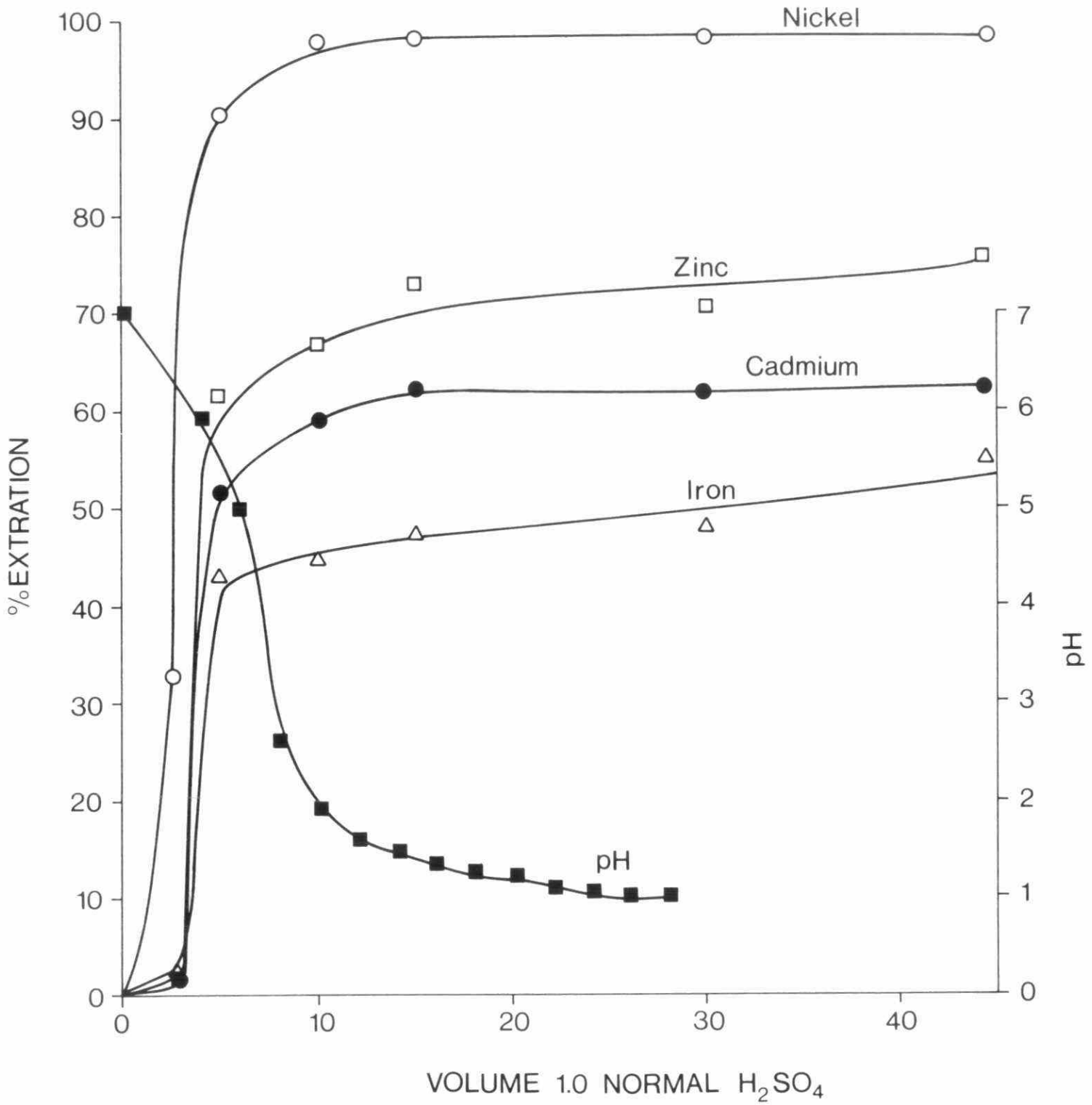

FIG. 7 METAL SOLUBILIZATION FROM MARKHAM SLUDGE WITH H_2SO_4

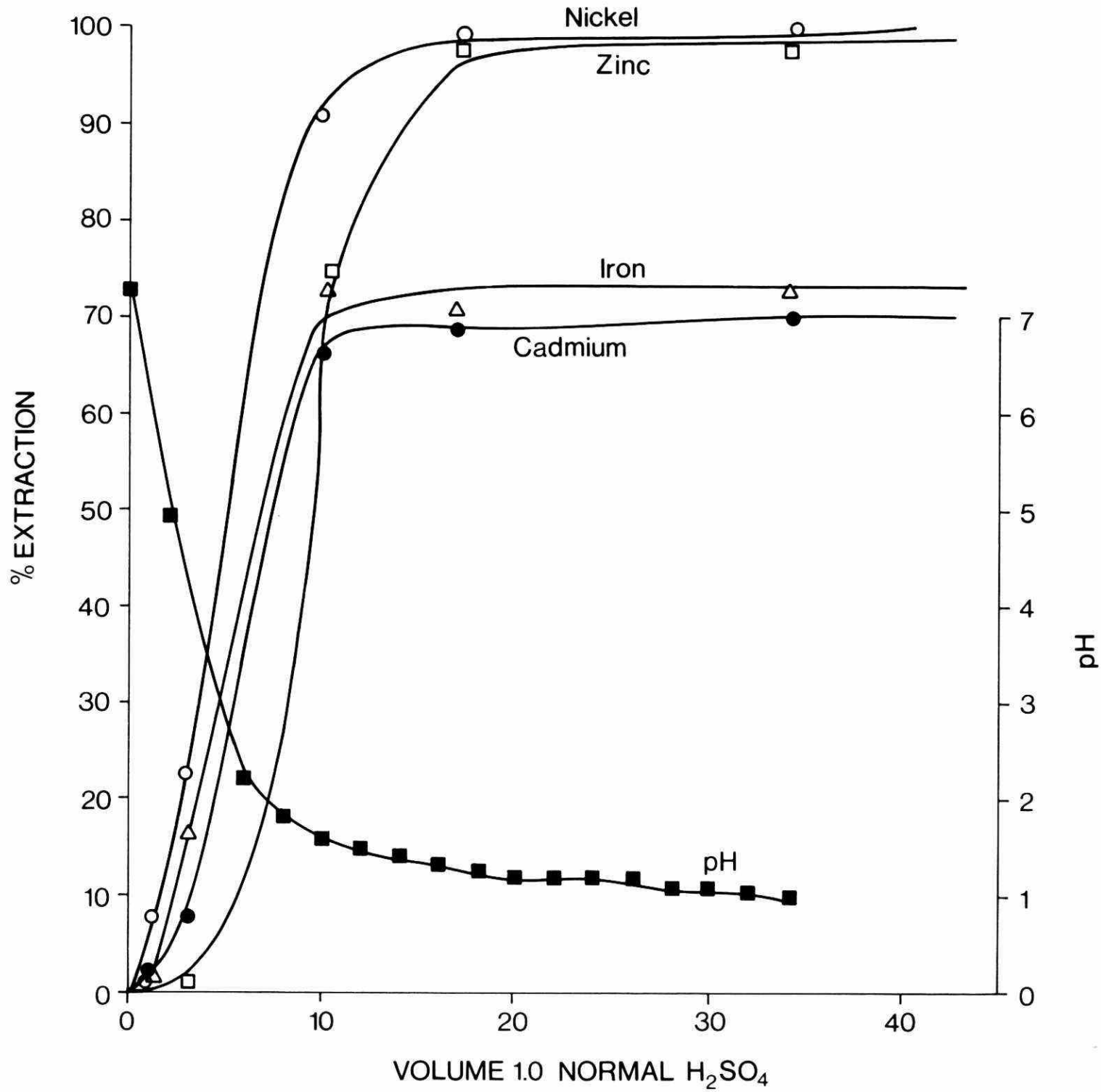

FIG. 8 METAL SOLUBILIZATION FROM AURORA SLUDGE WITH H_2SO_4

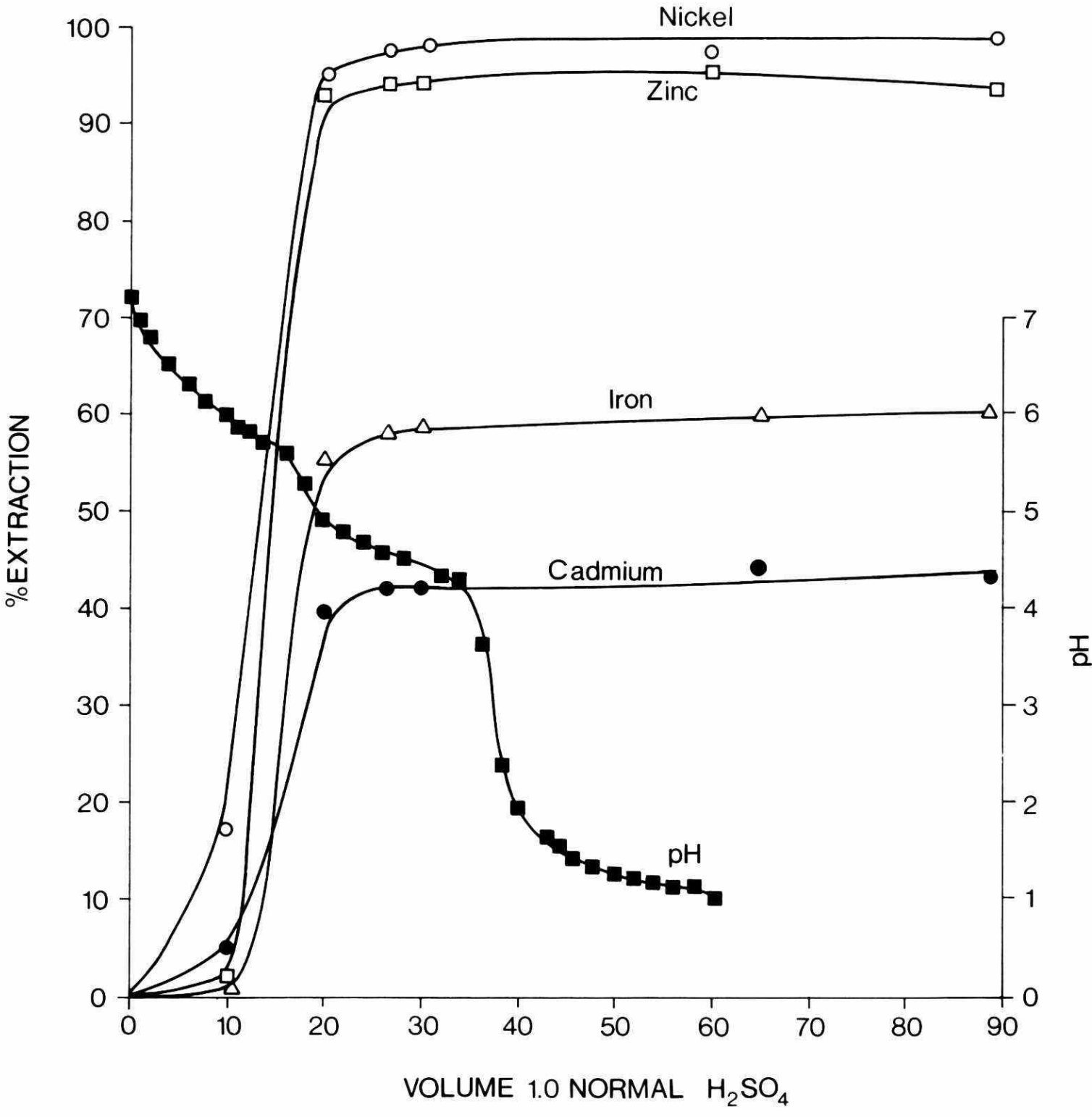

FIG. 9 METAL SOLUBILIZATION FROM NEWMARKET SLUDGE WITH H_2SO_4

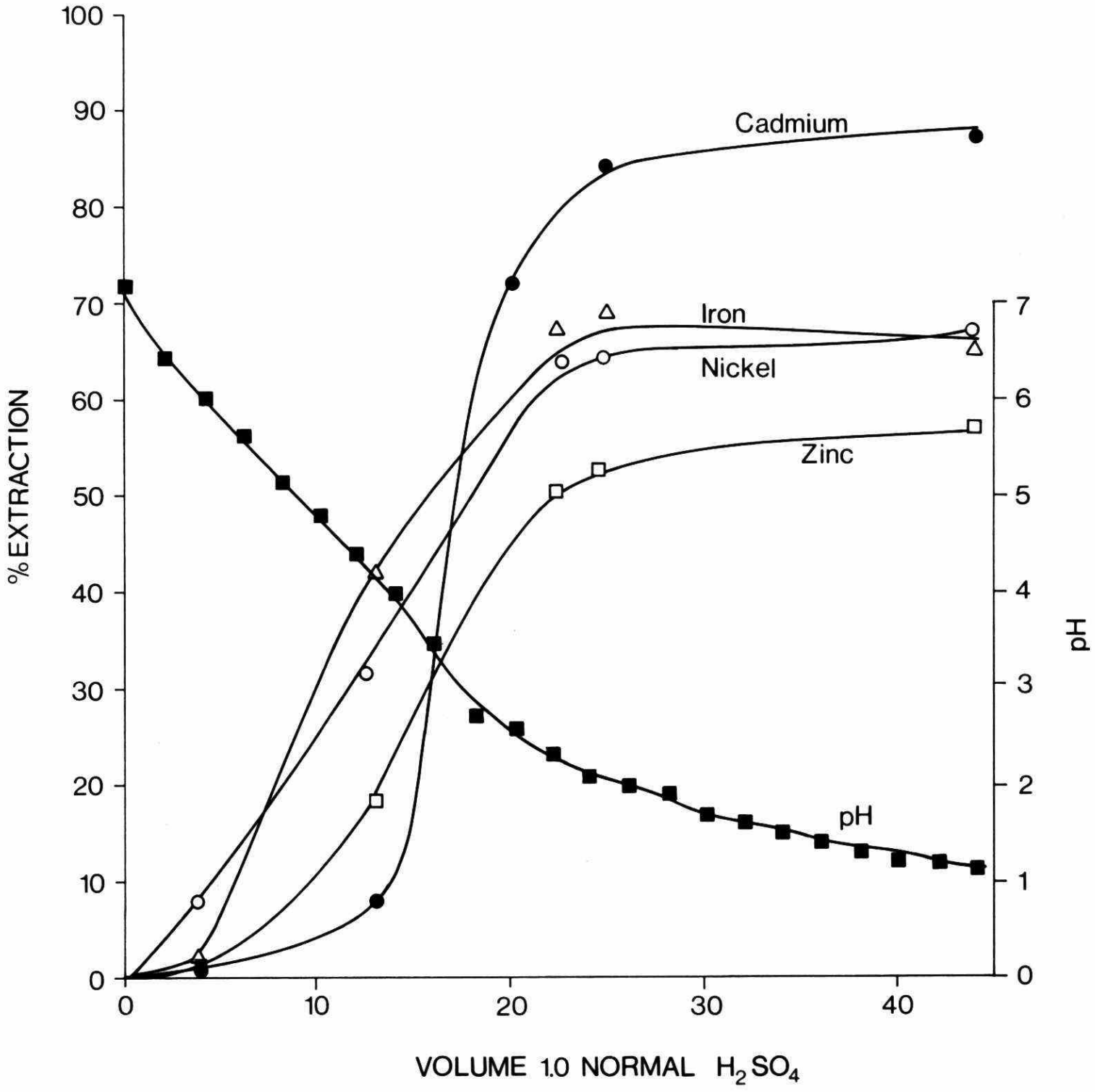

FIG. 10 METAL SOLUBILIZATION FROM GUELPH SLUDGE WITH H_2SO_4

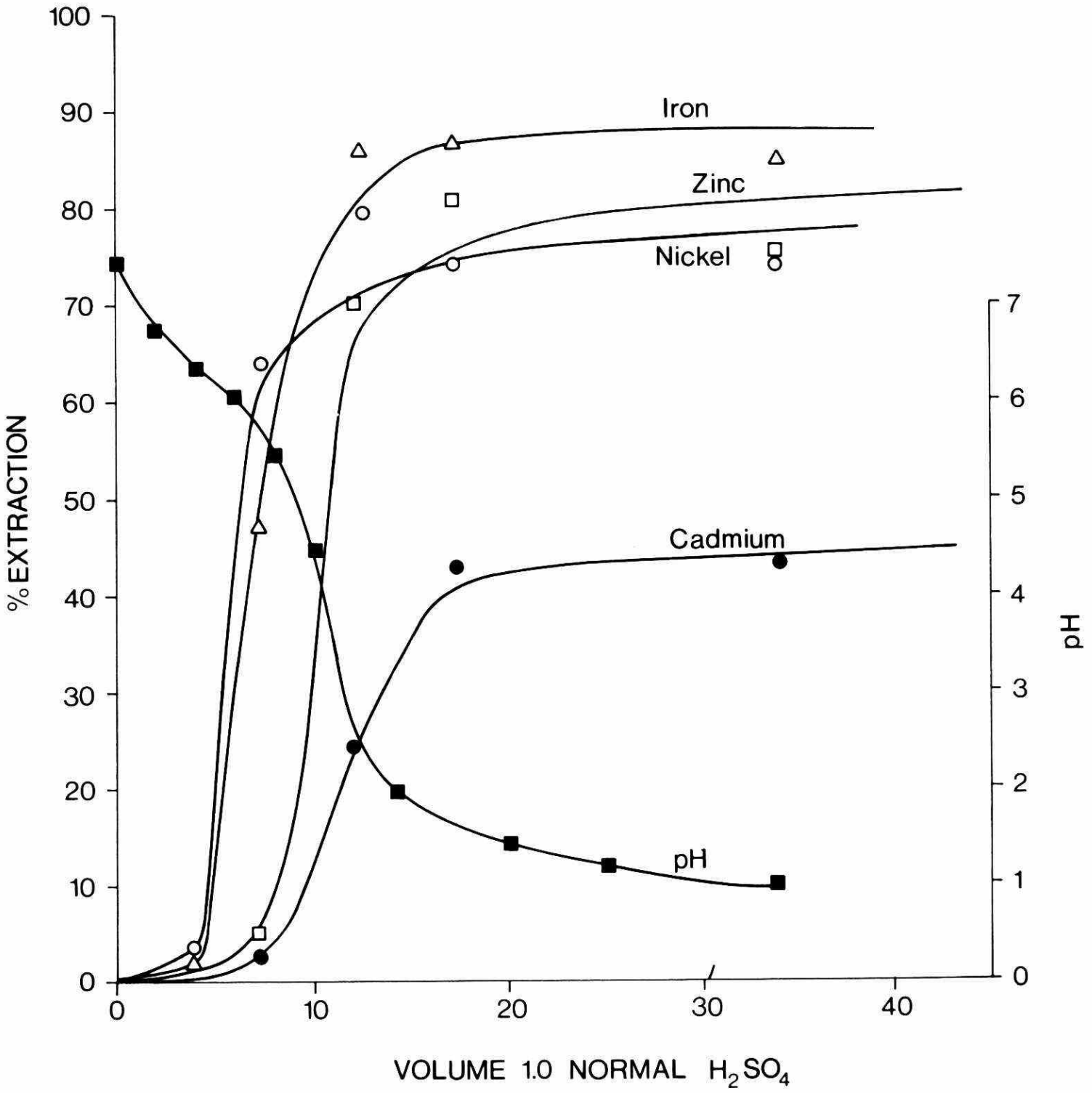

FIG. 11 METAL SOLUBILIZATION FROM FERGUS SLUDGE WITH H_2SO_4

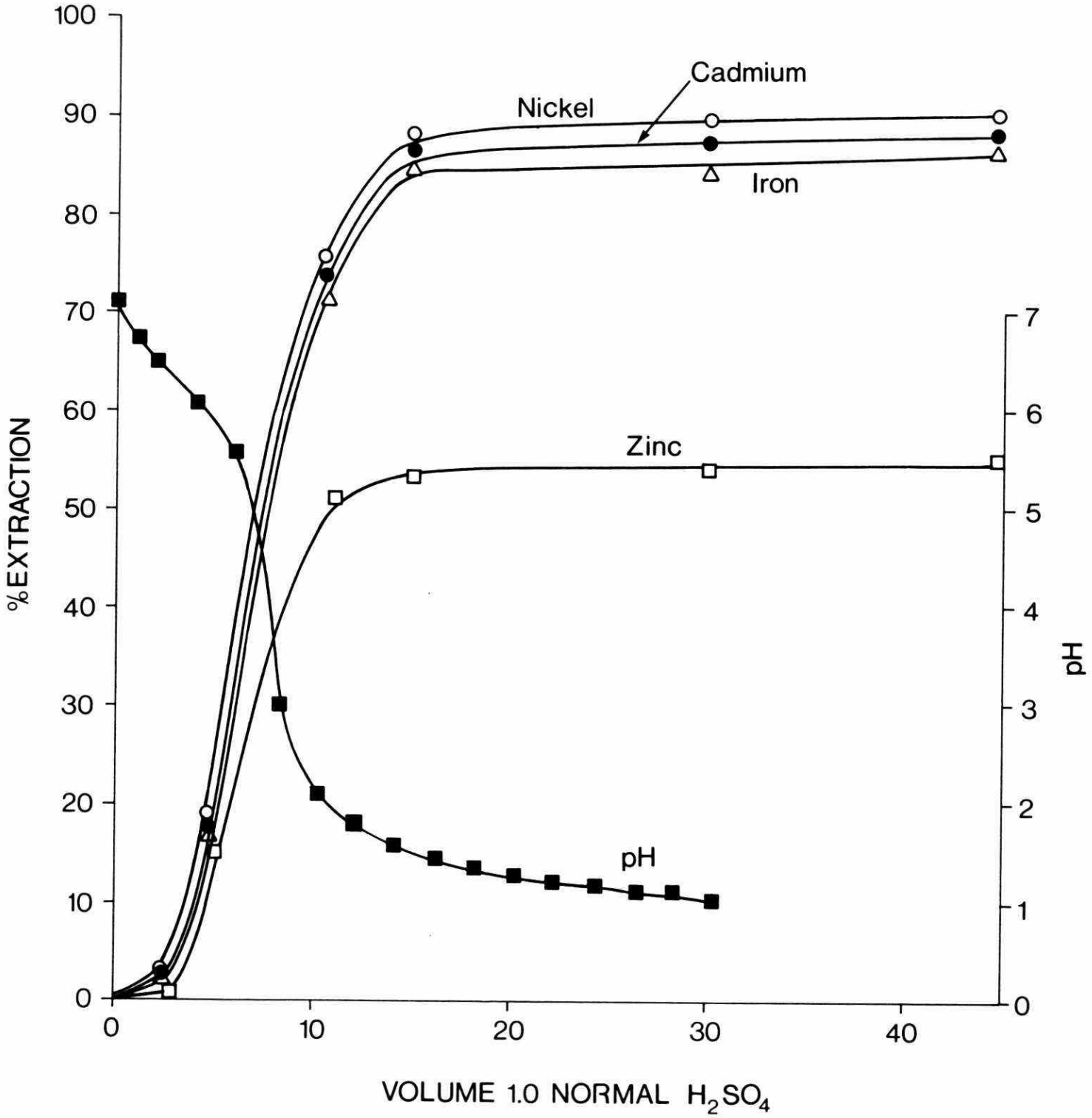

FIG. 12 METAL SOLUBILIZATION FROM BRANTFORD SLUDGE WITH H_2SO_4

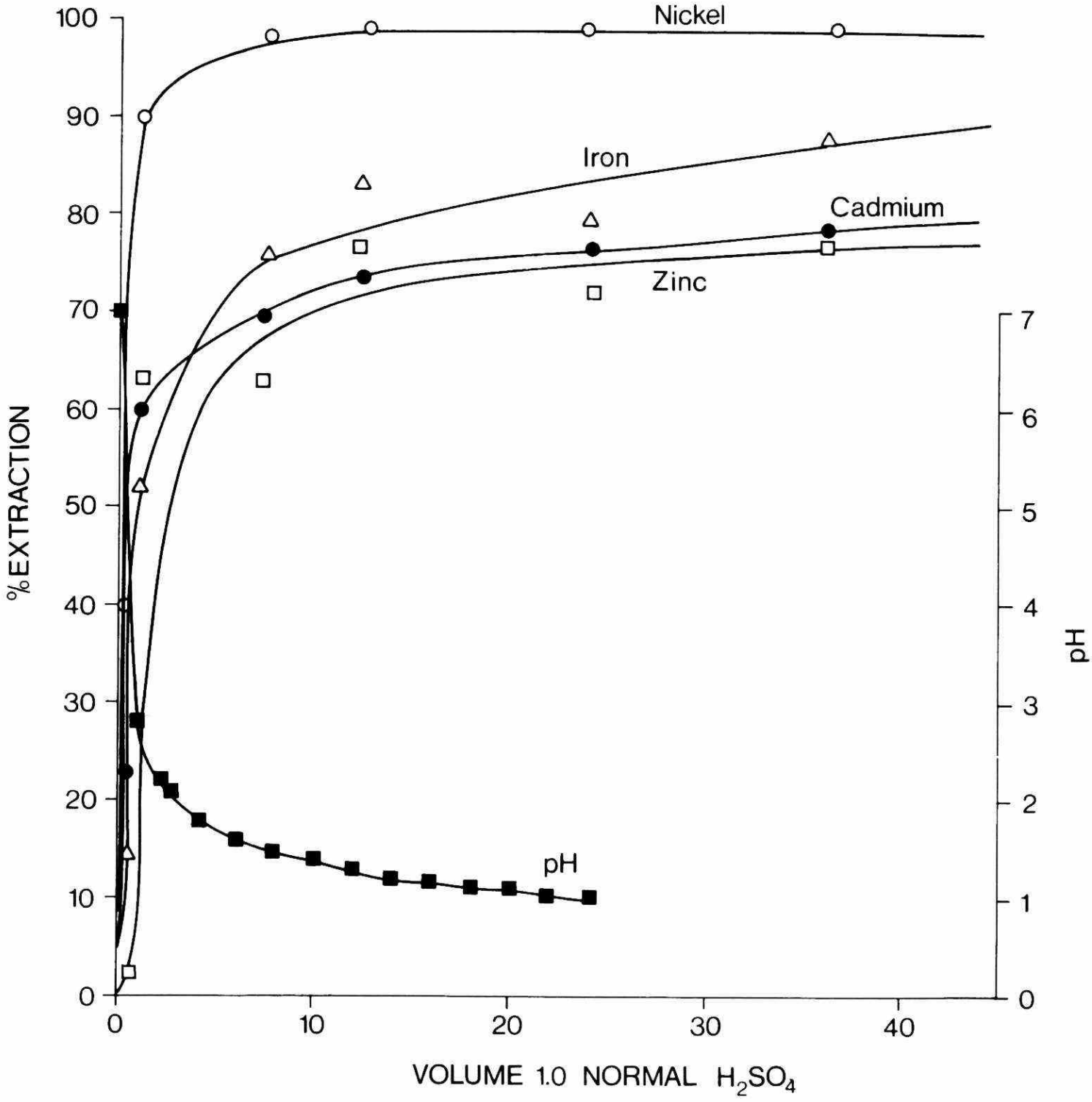

FIG. 13 METAL SOLUBILIZATION FROM DUNNVILLE SLUDGE WITH H_2SO_4

present is complexed to organic matter. $PbSO_4$ is only sparingly soluble so it is not surprising that H_2SO_4 does not extract much Pb from sludges, but there is no ready explanation for the poor Pb solubilization by HCl. About 2/3 of the iron in the sludges is also solubilized by the acid process, so this creates the difficult task of separating trace metals and phosphorus from Fe in the leachate.

On the suggestion of Ritcey and Ashbrook (28) an attempt was made to separate the trace metals from iron in the initial extraction step using NH_4OH and NH_4OH - $(NH_4)_2SO_4$. The NH_4OH - $(NH_4)_2SO_4$ extraction is used commercially in the mining industry to recover trace metals from ores (29, 30). Many metals such as Cu, Zn, Ni and Cd form soluble amine complexes, whereas others such as Fe, and Pb do not. This separation would make further processing of the leachate or remaining sludge for recovery purposes much easier. Data for the basic extraction of the various sludges are shown in Tables 9 to 16. The NH_4OH extraction was poor and was improved only slightly by increasing the free ammonia level with $(NH_4)_2SO_4$. Heating the solution to 80°C and bubbling oxygen into the system did not improve the extraction significantly. Even though the process works well for ores, the complexity and high organic content of the sludge system made it ineffective for digested sludge.

Since acid extraction seems to be the only way to remove many of the toxic constituents from sludge, cost calculations for the process were made. The quantities and costs of H_2SO_4 and HCl required for sludge leaching are shown in Tables 17 and 18, respectively. The costs per ton of dry sludge solids vary from $27 to $60 for H_2SO_4 and from $37 to $143 for HCl. The average cost is lower for H_2SO_4 than for HCl, $41 as opposed to $77, so H_2SO_4 would be the preferable acid.

The disposal of sludge represents one of the major expenses of sewage treatment facilities. The average sludge haulage costs in Ontario are $32 per ton of dry solids (7). If the proposed sludge detoxification method were adopted, and capital and labour costs of the process were omitted, the cost of H_2SO_4 alone would more than double sludge disposal costs. Any gain accrued by the recovery of phosphorus, zinc or iron would be minimal since processing of large volumes of dilute leachate would be expensive.

TABLE 9

THE EXTRACTION OF OAKVILLE SLUDGE (1.8% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Aluminum	146	11	9		
Cadmium	1.06	25	23	2	<2
Calcium	700	83	91		
Chromium	35.4	43	24		
Copper	40.2	<1	<1	2	<1
Iron	218	47	47	<1	1
Lead	23.1	6	7	1	3
Nickel	6.2	58	55	19	20
Zinc	194	67	57	1	14
Total Phosphorus	324	98	90		
Total Kjeldahl Nitrogen	1390	48	26		
Total Organic Carbon	4990	4	3		

TABLE 10

THE EXTRACTION OF MARKHAM SLUDGE (1.4% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	95.2	7	7		
Cd	0.32	63	88	<3	9
Ca	720	82	94		
Cr	1.64	48	39		
Cu	101	24	42	20	33
Fe	138	47	53	<1	1
Pb	10.4	43	93	1	11
Ni	0.18	99	99	<5	67
Zn	21.0	71	76	12	43
T.P.	244	90	90		
T.K.N.	1410	40	24		
T.O.C.	4140	11	10		

TABLE 11

THE EXTRACTION OF AURORA SLUDGE (2.1% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	762	91	30		
Cd	0.26	69	69	<8	8
Ca	1680	89	92		
Cr	192	81	10		
Cu	11.1	4	1	6	4
Fe	153	73	50	1	<1
Pb	5.1	47	8	<2	13
Ni	1.52	100	47	34	13
Zn	7.0	83	63	40	27
T.P.	392	64	6		
T.K.N.	904	11	19		
T.O.C.	3380	7	4		

TABLE 12

THE EXTRACTION OF NEWMARKET SLUDGE (1.1% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	42	9	1		
Cd	0.52	42	42	<4	<4
Ca	4270	16	82		
Cr	0.68	18	6		
Cu	4.2	49	1	17	9
Fe	97	58	2	<1	<1
Pb	3.0	36	15	<3	19
Ni	0.06	100	100	<30	<30
Zn	14.0	94	3	11	39
T.P.	296	61	54		
T.K.N.	904	19	21		
T.O.C.	1360	53	28		

TABLE 13

THE EXTRACTION OF GUELPH SLUDGE (4.2% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	934	[illegible]	45		
Cd	7.7	14	8	<1	<1
Ca	2580	28	93		
Cr	116	87	43		
Cu	90.8	<1	<1	<1	<1
Fe	1110	68	57	<1	<1
Pb	46.5	8	6	<1	2
Ni	3.1	69	65	9	14
Zn	274	56	49	<1	9
T.P.	1290	91	43		
T.K.N.	1610	35	28		
T.O.C.	8320	7	5		

TABLE 14

THE EXTRACTION OF FERGUS SLUDGE (2.8% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	90.8	19	21		
Cd	0.78	44	44	<3	<3
Ca	1350	62	95		
Cr	35.6	79	70		
Cu	127	<1	<1	<1	<1
Fe	1440	89	88	<1	2
Pb	15.0	17	17	<1	5
Ni	7.3	75	84	27	30
Zn	394	81	86	1	7
T.P.	690	95	95		
T.K.N.	1990	42	39		
T.O.C.	6440	5	4		

TABLE 15

THE EXTRACTION OF BRANTFORD SLUDGE (1.1% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	147	26	26		
Cd	0.62	87	84	3	<3
Ca	616	88	93		
Cr	15.4	75	62		
Cu	29.9	47	70	17	<1
Fe	848	85	92	<1	2
Pb	20.4	42	93	<1	4
Ni	3.9	88	88	27	29
Zn	63.0	53	57	3	16
T.P.	360	90	90		
T.K.N.	1590	48	31		
T.O.C.	3270	12	7		

TABLE 16

THE EXTRACTION OF DUNNVILLE SLUDGE (0.4% SOLIDS) WITH ACID AND BASE

ELEMENT	TOTAL CONCENTRATION (Wet Weight ppm)	% EXTRACTION			
		H_2SO_4 (pH 1.5)	HCl (pH 1.5)	NH_4OH (pH 13)	NH_4OH-$(NH_4)_2SO_4$ (pH 13)
Al	92.2	4	5		
Cd	0.20	70	80	<10	<10
Ca	177	67	72		
Cr	0.72	17	14		
Cu	1.14	19	23	47	25
Fe	153	78	77	<1	<1
Pb	0.3	100	100	<30	100
Ni	0.06	100	100	<30	<30
Zn	3.4	65	71	5	44
T.P.	184	21	21		
T.K.N.	636	6	6		
T.O.C.	900	30	33		

TABLE 17

QUANTITIES AND COSTS OF SULPHURIC ACID REQUIRED FOR LEACHING SLUDGES

SLUDGE	VOLUME H_2SO_4 /g dry solids (ml)	VOLUME H_2SO_4 /ton dry solids (Imp. gallons)	COST H_2SO_4* /ton dry solids ($)	COST H_2SO_4* /million gallons + influent ($)
Oakville	0.33	66	27	16
Markham	0.43	86	36	22
Aurora	0.48	96	40	24
Newmarket	0.73	146	60	36
Guelph	0.36	72	30	18
Fergus	0.39	78	32	19
Brantford	0.55	110	46	28
Dunnville	0.68	136	56	34

* Industrial H_2SO_4 in tank trucks costs 45^{00} per ton.

+ Assuming 1200 lb of dry sludge solids per million gallons of influent.

TABLE 18

QUANTITIES AND COSTS OF HYDROCHLORIC ACID REQUIRED FOR LEACHING SLUDGES

SLUDGE	VOLUME HCl /g dry solids (ml)	VOLUME HCl* /ton dry solids (Imp. gallons)	COST HCl* /ton dry solids ($)	COST HCl* /million gallons + influent ($)
Oakville	0.67	134	48	29
Markham	0.86	172	62	37
Aurora	0.52	104	37	22
Newmarket	2.0	400	143	86
Guelph	0.62	124	44	26
Fergus	1.14	227	81	49
Brantford	1.45	289	104	62
Dunnville	1.36	271	97	58

* Industrial HCl costs in tank trucks 60^{00} per ton.

\+ Assuming 1200 lb of dry sludge solids per million gallons of influent.

3.3 Sludge Incinerator Ash Leaching

Since removal and recovery of metals or phosphates from wet sludge is not economically feasible, it was decided to study the processing of sludge incinerator ash. Removal of the organic component by incineration leaves the metals in a more concentrated form which should make leaching processes more efficient. In addition, the ash should be easier to handle and to separate from extraction liquors than wet sludge. Ashes from several locations, as well as ashes resulting from sludge incineration at various temperatures were studied. The results of the ash analysis for several metals and for phosphorus are shown in Table 19. As expected, metal and phosphorus concentrations were considerably higher in the ash than in the wet sludge.

It has been suggested that heavy metals leach out of the ash even with neutral distilled water (14). To see what portion of the metals in the ashes are available for leaching, the acetic acid extractable metal was determined (Table 20). The available metal changed with source and incineration temperature. The London incinerator ash had the highest proportion of available metals, but it also had the lowest metal levels. The available metal changed significantly when Hamilton sludge was incinerated at various temperatures. From these limited data it appears that it should be possible to minimize the environmental impact of landfilling incinerator ash by proper adjustment of incineration conditions. If this is the case, the removal and recovery of ash constituents should be attempted only when a positive economic benefit can be ascertained.

Cambrian Processes Ltd. (14) recommended the use of 60% H_2SO_4 for the extraction of valuable ash constituents because a separation of iron from the other heavy metals and phosphorus was obtained with this concentration. Fowlie (31) confirmed this separation and suggested that iron is dissolved by boiling 60% H_2SO_4, but precipitates when the acid cools down before filtration. An integral part of the Campro process is ion exchange to remove cations from the 60% acid leach. No recommendations for ion exchange resin were made and the resulting search in the present study failed to find any which could function in 60% H_2SO_4.

TABLE 19

THE ANALYSIS OF SLUDGE INCINERATOR ASHES

(Micrograms Per Gram)

ASH	Cd	Cu	Fe	Pb	Ni	Zn	P
Hamilton	29.3	2,930	146,000	3,610	800	18,200	53,900
London	9.6	575	61,000	173	330	1,340	28,600
Hamilton * (760°C)	47.9	2,400	120,000	3,260	670	14,400	41,500
Hamilton * (820°C)	29.6	2,570	133,000	2,770	710	15,500	45,900
Hamilton * (870°C)	19.7	2,960	143,000	3,450	790	16,600	53,300
Hamilton * (930°C)	19.5	2,440	112,000	1,850	600	12,600	51,800
Borden * (760°C)	18.8	1,130	43,000	830	290	4,140	56,600

* These sludges were incinerated in the Environmental Protection Service experimental incinerator at Borden, Ontario.

TABLE 20

PERCENTAGE OF AVAILABLE HEAVY METALS IN SLUDGE INCINERATOR ASHES

ASH	Cd	Cu	Fe	Pb	Ni	Zn
Hamilton	17	3	<0.1	<0.5	3	5
London	30	14	0.4	<7	35	33
Hamilton* (760°C)	17	1	0.3	1	3	16
Hamilton* (820°C)	14	0.1	1.2	1	5	12
Hamilton* (870°C)	20	0.1	0.2	<0.5	3	2
Hamilton* (930°C)	<10	1	0.3	<0.5	3	9
Borden* (760°C)	27	0.4	3	2	3	6

* These sludges were incinerated in the Environmental Protection Service experimental incinerator at Borden, Ontario.

Other separation techniques such as reverse osmosis also suffer from the same inability to function at this acid level. Distillation of the acid for reuse seems the only reasonable separation process.

As an alternative, a counter current type process was examined in which the acid would be consumed in the extraction process. Table 21 shows the percent extraction of the various metals in the incinerator ashes with 60% sulphuric acid. A 5:1 dilution was performed on the hot acid leach prior to filtration to prevent reprecipitation. As shown, iron was efficiently extracted in almost all cases. The effect of changing the sulphuric acid concentration on the extraction of normal Hamilton ash is shown in Figure 14. It can be seen that when a dilution is made to prevent reprecipitation, over 90% of the phosphorus as well as most of the Cd, Cu, Fe, Ni and Zn are solubilized by the acid mixtures.

To determine the acid requirement for ash extraction, various H_2SO_4 to ash ratios were tested (Table 22). The extraction efficiency of the acid slowly decreased and the H_2SO_4 was gradually consumed as the acid to ash ratio decreased. The best H_2SO_4 extraction procedure would be to treat the ash in a series of sulphuric acid baths, with the objective of extracting the majority of valuable ash constituents and, at the same time, use up most of the sulphuric acid. However, some acid residual is required or else the metals begin to precipitate. Calculations show that to extract at least 66% of the Cd, Cu, Fe, Ni, Zn and phosphorus from the ash approximately 50 Imp. gallons of concentrated sulphuric acid per ton of ash would be required. At an acid cost of $45 per ton, this corresponds to an expenditure of $21 per ton of ash treated.

Attempts were made to separate the trace metals and phosphorus from the iron by extracting the ash with the NH_4OH - $(HN_4)_2SO_4$ procedure already described. The best extractions were obtained with a boiling mixture of NH_4OH - $(NH_4)_2SO_4$ at pH 9.0 and are: Cd, 40%; Cu, 16%; Fe, 0.4%; Pb, 16%; Ni, 15%; and Zn, 15%. These extractions are slightly better than those obtained with wet sludge and there is a separation between iron and the other metals, but they were not encouraging enough to justify further work.

TABLE 21

PERCENTAGE EXTRACTION OF ASH METALS WITH 60% SULPHURIC ACID

ASH	Cd	Cu	Fe	Pb	Ni	Zn
Hamilton	79	87	93	5	71	79
London	<20	62	24	9	74	69
Hamilton* (760°C)	45	78	38	5	72	91
Hamilton* (820°C)	37	94	54	8	63	87
Hamilton* (870°C)	28	75	80	6	80	93
Hamilton* (930°C)	29	86	91	7	62	100
Borden* (760°C)	27	76	71	12	47	88

* These sludges were incinerated in the Environmental Protection Service experimental incinerator at Borden, Ontario.

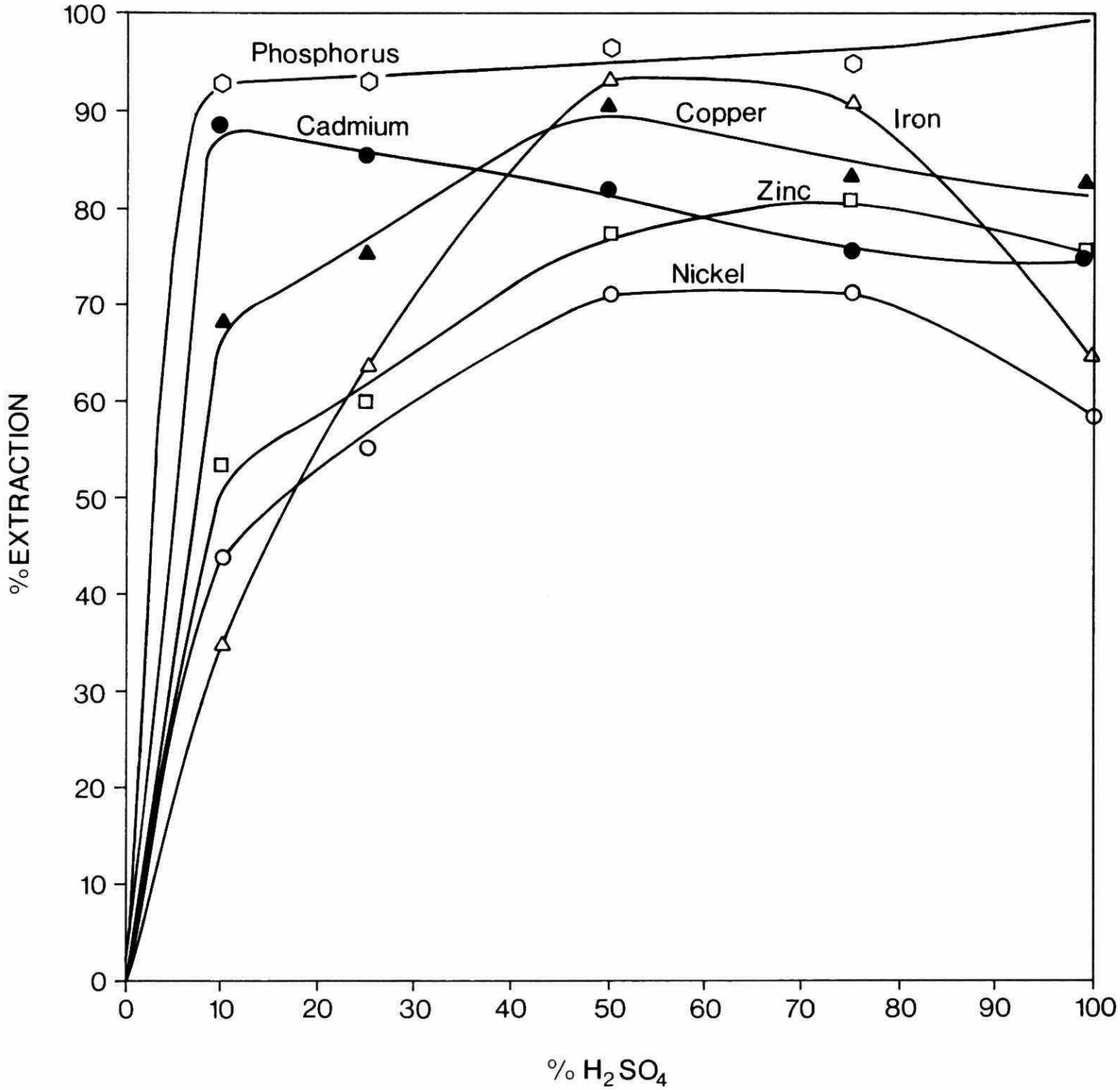

FIG. 14 SOLUBILIZATION OF HAMILTON INCINERATOR ASH CONSTITUENTS WITH H_2SO_4 – H_2O MIXTURES

TABLE 22

PERCENTAGE EXTRACTION OF ASH METALS WITH DIFFERENT QUANTITIES OF SULPHURIC ACID

ml Conc. H_2SO_4 /g ash	% EXTRACTION					Acid Consumed (%)
	Cd	Cu	Fe	Ni	Zn	
12.5	82	90	93	71	77	<1
2.5	75	92	84	72	74	2
1.25	46	82	75	74	85	9
0.83	38	77	64	68	68	20
0.63	34	67	58	57	58	22
0.50	27	63	55	55	55	28
0.14	60	31	6	11	17	63

3.4 Metal and Phosphorus Recovery Schemes

On the average, 52 lb of iron, 47 lb of phosphorus, 12 lb of zinc, 5 lb of copper and lesser amounts of other trace metals per ton of dry matter were found in the wet sludges studied. To recover these materials, about 50 tons of wet sludge would have to be processed. Removal and recovery is just not practical for this large volume of dilute raw material. On the other hand, one ton of sludge incinerator ash contained, on the average, 216 lb of iron, 95 lb of phosphorus, 24 lb of zinc, 4 lb of copper and other trace metals. The recovery of these values may be economically feasible. The phosphate value of the ash is currently about $46 per ton (14). It is doubtful whether the recovery of iron, which is fairly inexpensive, would prove profitable, but the recovery of zinc and copper could marginally improve the cost evaluation.

The extraction of incinerator ash with sulphuric acid has already been described (Section 3.3). The next stage of the recovery process would be to neutralize the hot H_2SO_4 leachate. The iron, copper and zinc levels at various pH's are shown as the H_2SO_4 leachate is titrated with NH_4OH (Figure 15). It can be seen that all the metals are precipitated by the time pH reaches 7, but that zinc and copper are resolubilized when the pH becomes greater than 7. This is because both metals form soluble amine complexes in alkaline solutions. Nickel and cadmium are also redissolved by the formation of amine complexes and phosphorus is redissolved as the iron in the mixture is converted to the oxide. Iron oxide remains in the solid phase. The conditions during the titration (Figure 15) were not optimized but it should be possible to redissolve most of the Zn, Cu, Ni, Cd and phosphorus by heating the solution and adding $(NH_4)_2SO_4$ to increase the free ammonia concentration. Because of the high cost of NH_4OH, a two stage process should also be considered. The acid leachate could be neutralized with less expensive NaOH. The resulting precipitate could then be separated from the Na_2SO_4 solution by filtration or sedimentation and extracted with hot NH_4OH - $(HN_4)_2SO_4$. This process should be just as effective and would result in large reagent cost savings.

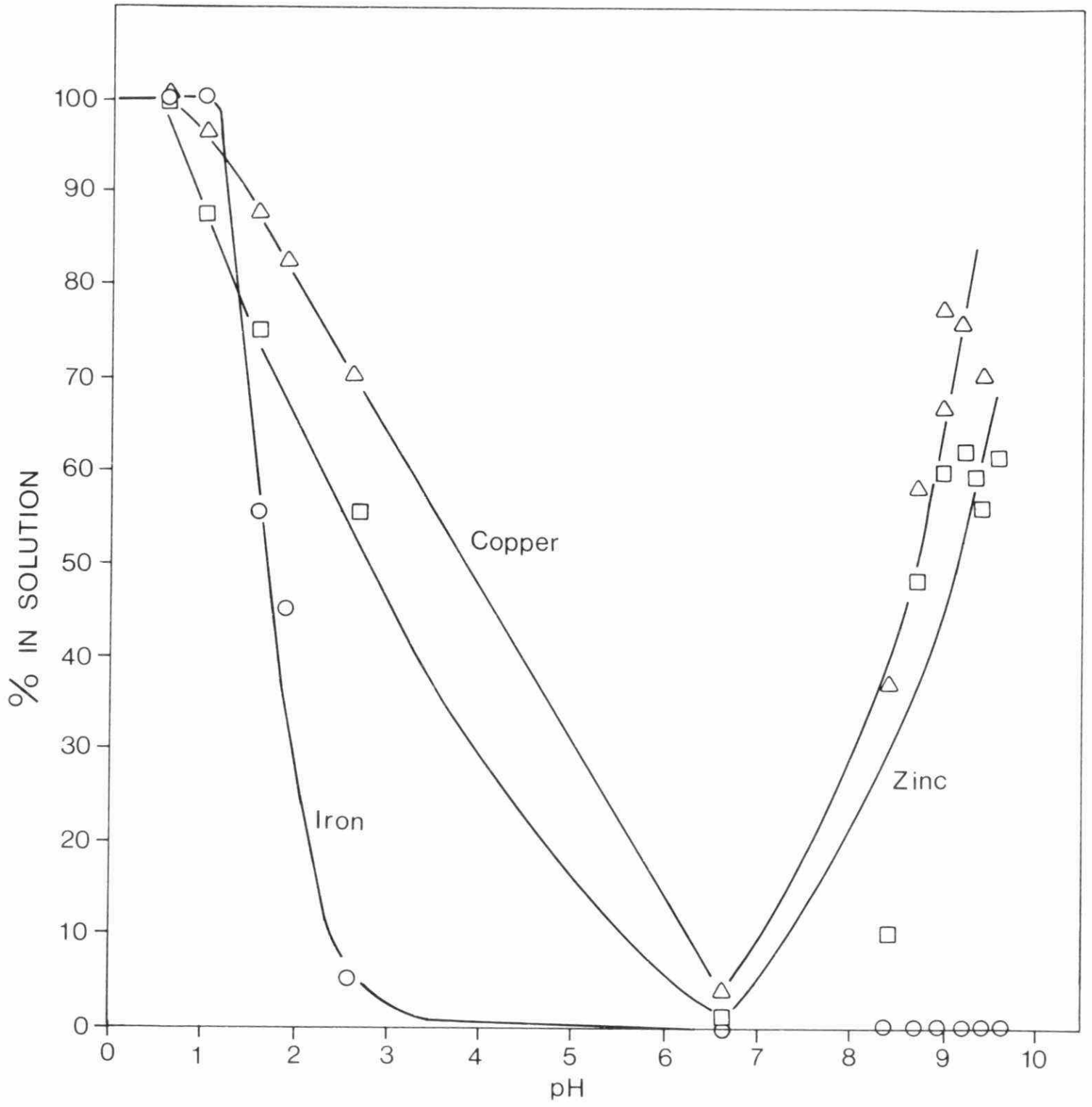

FIG. 15 TITRATION OF H_2SO_4 INCINERATOR ASH LEACHATE WITH NH_4OH

Further processing of the NH_4OH - $(NH_4)_2SO_4$ leachate would be carried out electrochemically to first remove the copper and then remove the zinc, nickel and cadmium. A final ion exchange step may prove necessary for effluent polishing. Ammonium phosphate can be recovered from the ammonia leach after electrolysis. A flow chart for the process is shown in Figure 16. This procedure worked reasonably well for Hamilton incinerator ash but more detailed studies are required on ashes of various compositions to see whether the process is generally applicable.

The sulphuric acid costs per ton of ash for the process are about $21 and the price of sodium hydroxide (@ $18/cwt) for neutralization of the partially spent acid would be of the order of $2. The costs of the NH_4OH and $(NH_4)_2SO_4$ would bring the total reagent to over half the value of the recoverable ash constituents. Capital purchases for the extraction and electrochemical equipment would be fairly high and labour charges could further increase process expenditures to roughly the break-even point.

Insufficient time was available for a detailed economic examination of this recovery process. However, order of magnitude numbers would indicate that the procedure is probably not economically feasible. For very large quantities of ash like those produced by incinerating the sludge of Metroploitan Toronto, the quantities of recoverable metals and phosphates may warrant a thorough economic evaluation, but for smaller operations, the likelihood that profitable recycle could be undertaken is slight.

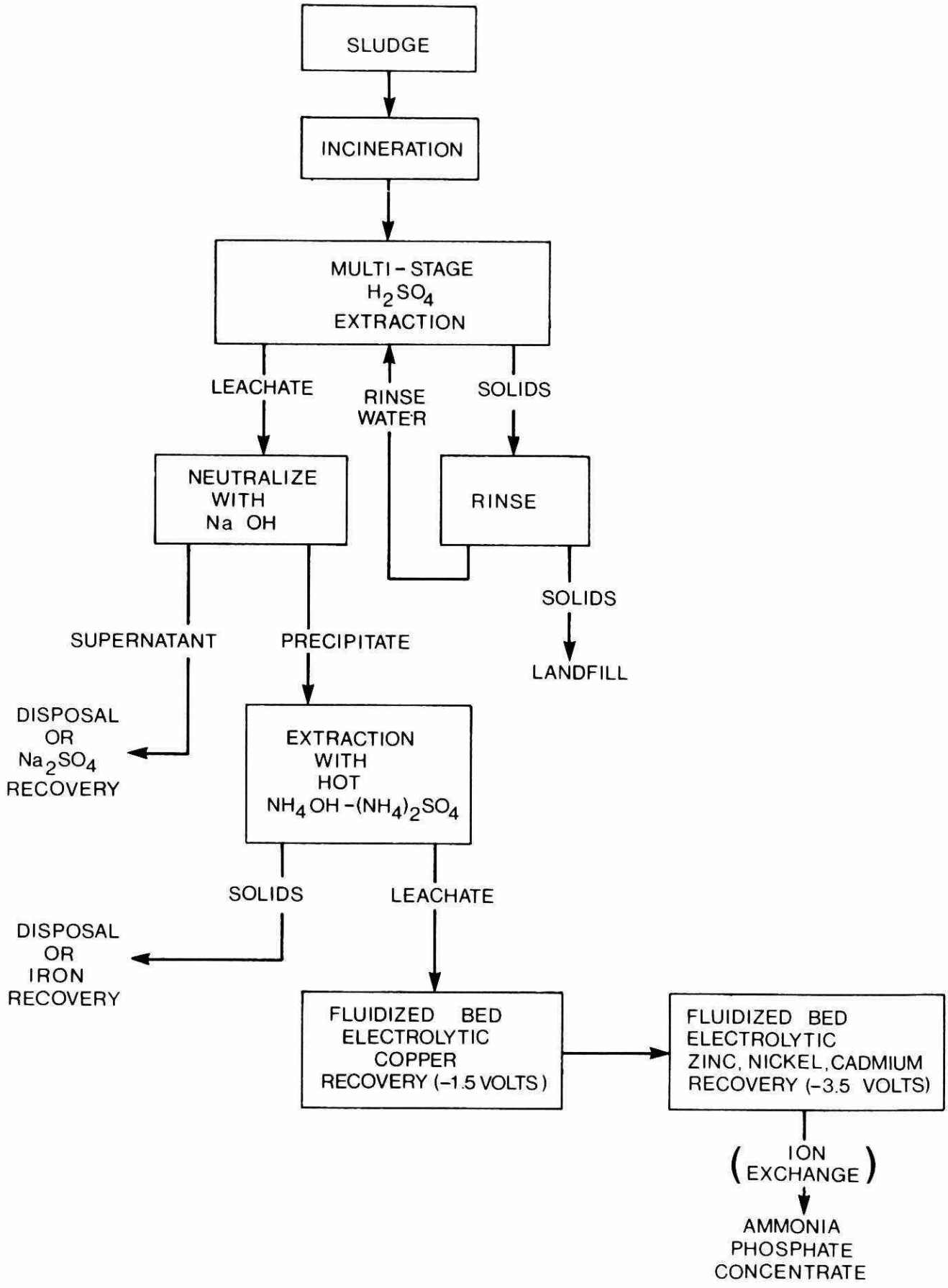

FIG. 16 PROCESS FLOW CHART

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